

For Reference

---

**NOT TO BE TAKEN FROM THIS ROOM**

# For Reference

NOT TO BE TAKEN FROM THIS ROOM

EX LIBRIS  
UNIVERSITATIS  
ALBERTAENSIS











THE UNIVERSITY OF ALBERTA

METHYLATION OF METALATED INDENE AND ACENAPHTHENE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

DOCTOR OF PHILOSOPHY

BY

ANTHONY BOSCH, B.Sc.

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

NOVEMBER, 1965



THE UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to  
the Faculty of Graduate Studies for acceptance, a thesis entitled

METHYLATION OF METALATED INDENE AND ACENAPHTHENE

submitted by Anthony Bosch, B. Sc., in partial fulfilment of the  
requirements for the degree of Doctor of Philosophy.



## ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks and appreciation to Dr. R. K. Brown, whose valuable guidance and encouragement made this work possible.

Thanks also are extended to:

Mr. R. N. Swindlehurst and Mrs. Gail B. Conway for measuring the infrared and nuclear magnetic resonance (A-60) spectra; Mr. G. Bigam for measuring the HR-100 nuclear magnetic resonance spectra; Messrs. R. Taylor and W. Duholke for the mass spectrometer analyses; and Miss Darlene Roberts for performing some of the microanalyses.

Mrs. Gail B. Conway for typing this manuscript.

Mr. Brian Brownlee for the assistance in the preparation and investigation of some of the tri- and tetrasubstituted acenaphthenes (Compounds XCIX - CI, CVI).

The Cities Services Research and Development Company and the National Research Council of Canada for the receipt of scholarships.

The University of Alberta for financial assistance and the award of a Dissertation Fellowship.

Dr. R. K. Brown for financial assistance during the latter part of this work.

Dr. R. B. Sandin for many stimulating and encouraging discussions.



## ABSTRACT

The metalation of indene and acenaphthene by the alkali metals lithium and potassium, and the reaction of the resulting organometallic derivatives with excess methyl iodide has been studied. The metalation of fluorene also has been reinvestigated.

The reaction of metallic lithium and potassium with indene and fluorene in refluxing 1,2-dimethoxyethane yielded reduction products of indene and fluorene, 1-metalated indene, and 9-metalated fluorene, and as well was accompanied by the production of some hydrogen gas due to the acidic methylene group. The amount of hydrogen was small for fluorene but quite substantial for indene.

Metalation of indene, 1-methylindene, and 3-methylindene in refluxing 1,2-dimethoxyethane, followed by methylation of these metalated indenenes at 0°, gave a mixture consisting of starting material, the corresponding indan, monomethylindene, dimethylindene, and in some cases trimethylindene. Two competing reaction mechanisms resulting in the formation of the metalated indenenes are suggested, and possible routes for the formation of the di- and trimethylindenenes were examined.

The reaction of acenaphthene with one equivalent of potassium metal and one or two equivalents of lithium metal in refluxing 1,2-dimethoxyethane produced little hydrogen gas, but the use of two gram-equivalents of potassium gave a substantial amount of hydrogen. Decomposition of the



metalation products with aqueous acid gave three to five products which consisted mainly of starting material, and contained some reduction products as well. Metalation at room temperature with potassium yielded four products, one of which was a dihydroacenaphthene.

Metalation of acenaphthene with potassium followed by methylation gave a mixture consisting of at least eleven products. These were starting material, monomethylacenaphthene, as well as reduction products and more highly-alkylated products. Similar reactions with lithium metal resulted in very little alkylation. The resulting mixture, containing six to seven products, was made up largely of starting material.

The synthesis of six C<sub>1</sub>- and C<sub>2</sub>-methylacenaphthenes and four reduced acenaphthenes was undertaken by conventional organic methods. The preparation of 1,1,2,2-tetramethylacenaphthene led to some anomalous reactions, for which possible mechanisms are postulated.



## TABLE OF CONTENTS

Acknowledgements	iii
Abstract	iv
List of Tables	x
List of Figures	xi

## INTRODUCTION

A. The Problem	1
B. Literature Survey	2
1. The Indene System	4
(i) Acidity of Indene	4
(ii) Metalations and Subsequent Reactions	6
(iii) Isomerization in the Indene Ring System	14
(iv) Synthesis of the Indene Nucleus	17
2. The Acenaphthene System	21
(i) General Nature of the Acenaphthene Molecule, and the Reactivity of the Methylene Groups	21
(ii) Synthesis of the Acenaphthene Nucleus	28
3. The Solvent Role in Metalation	30
4. The Nature of Organometallic Compounds	32
5. Analytical Methods	35



## RESULTS AND DISCUSSION

### Part I - Indene

A. The Preparation of Methylindenes	37
B. Concerning the Mechanism of Metalation	46
C. Methylation of Indenyllithium and Indenylpotassium	54
1. Consumption of Metal	55
2. Formation of Indan	55
3. Recovered Starting Material	60
4. Formation of Monomethylindenes	61
(i) Thermal Isomerization of 1-Methylinde	62
(ii) Base-catalyzed Isomerization of 1-Methylinde	66
5. Formation of Dimethylindenes	74
Possible Routes Leading to Dimethylindenes	74
D. Alkylation of the Product Obtained from Metalation of Indene with Two Equivalents of Metal	85
E. Metalation and Alkylation of Both 3-Methylinde and 1-Methylinde	85

### Part II - Acenaphthene

F. The Preparation of Methylacenaphthenes	90
G. The Preparation of Hydrogenated Acenaphthene Derivatives	119
H. The Metalation of Acenaphthene	127
I. Methylation of Metalated Acenaphthene	137



## EXPERIMENTAL

A. Analyses by Gas-Liquid Chromatography (GLC) and Product Identification	157
B. Solvents and Chemicals	158
C. Experimental Work Concerned with the Preparation of Methylated Indenes and Indan	159
D. General Procedure for the Formation and Collection of Hydrogen Gas	172
E. General Procedure for the Metalation and Methylation of the Indenes	174
F. Analysis of Indenes on GLC Columns	175
G. The Stability of the Monomethylindenes	176
H. Consumption of Excess Metal. Possible Basic Sources Leading to Polyalkylation	178
I. Experimental Work Concerned with the Preparation of Methylated Acenaphthenes	182
J. Experimental Work Concerned with the Preparation of Reduced Acenaphthenes	216
K. The Stability of the Dihydroacenaphthenes	225
L. Preparation of 1,8-Dimethylnaphthalene	227
M. The Metalation of Acenaphthene. General Procedure for the Formation and Collection of Hydrogen Gas	228



N. General Procedure for the Metalation and Methylation of Acenaphthene	230
O. Analysis of Acenaphthenes on GLC Columns	230

BIBLIOGRAPHY	232
--------------	-----



LIST OF TABLES

I	Production of Hydrogen During the Reaction of Indene or Fluorene with Lithium or Potassium Metal in Refluxing 1,2-Dimethoxyethane (DME).	48
II	Preparation and Methylation of 1-Indenyllithium and 1-Indenylpotassium in 1,2-Dimethoxyethane.	56
III	Isomerization of Refluxing 1-Methylindene to 3-Methylindene.	63
IV	Isomerization of Refluxing 3-Methylindene to 1-Methylindene.	65
V	Isomerization of 1-Methylindene in the Presence of Base.	68
VI	Base-catalyzed Rearrangement of 1-Substituted Indenes in Pyridine Solution at 30° C.	73
VII	Results of the Methylation of 1-Indenyllithium and 1-Indenylpotassium Prepared by Treatment of Indene with Two Equivalents of the Metal	86
VIII	Metalation and Subsequent Methylation of 3-Methylindene in DME.	88
IX	Metalation and Subsequent Methylation of 1-Methylindene in DME.	89
X	Comparison of UV Absorptions of Reduced Acenaphthenes with Reduced Naphthalenes and Styrene Derivatives	126
XI	Production of Hydrogen During the Reaction of Acenaphthene with Lithium or Potassium Metal in Refluxing 1,2-Dimethoxyethane (DME).	129



LIST OF FIGURES

Fig. 1	NMR Spectrum of 1-Methylindene	143
Fig. 2	NMR Spectrum of 3,3-Dimethyl-1-indanol	143
Fig. 3	NMR Spectrum of 1,1-Dimethylindene	144
Fig. 4	NMR Spectrum of 3-Methylindene	144
Fig. 5	NMR Spectrum of 1,3-Dimethylindene	144
Fig. 6	NMR Spectrum of 1,1,3-Trimethylindene	145
Fig. 7	NMR Spectrum of 2-Methyl-1-acenaphthenone oxime	145
Fig. 8	NMR Spectrum of 2,2-Dimethyl-1-acenaphthenone oxime	145
Fig. 9	NMR Spectrum of 1-Methylacenaphthene	146
Fig. 10	NMR Spectrum of <u>cis</u> - and <u>trans</u> -1,2-Dimethyl-1-acenaphthenol	146
Fig. 11	NMR Spectrum of <u>cis</u> -1,2-Dimethylacenaphthene	146
Fig. 12	NMR Spectrum of <u>cis</u> - and <u>trans</u> -2-Methyl-1-acenaphthenol	147
Fig. 13	NMR Spectrum of <u>cis</u> - and <u>trans</u> -2-Methyl-1-bromoacenaphthene	147
Fig. 14	NMR Spectrum of 1,2,2-Trimethyl-1-acenaphthenol	147
Fig. 15	NMR Spectrum of 2,2-Dimethyl-1-methyleneacenaphthene	148
Fig. 16	NMR Spectrum of 2,2-Dimethyl-1-hydroxymethylacenaphthene	148
Fig. 17	NMR Spectrum of 1,1,2-Trimethylacenaphthene	148
Fig. 18	NMR Spectrum of 2,2-Dimethyl-1-methyleneacenaphthene oxide	149



Fig. 19	NMR Spectrum of 2,2-Dimethyl-1-acenaphthenecarboxaldehyde	149
Fig. 20	NMR Spectrum of 1,2,2-Trimethyl-1-acenaphthenecarboxaldehyde	149
Fig. 21	NMR Spectrum of 1,2,2-Trimethyl-1-acenaphthenecarboxaldehyde <u>p</u> -toluenesulfonylhydrazone	150
Fig. 22	NMR Spectrum of 1,2,2-Trimethyl-1-hydroxymethylacenaphthene	150
Fig. 23	NMR Spectrum of 1,2,2-Trimethyl-1-hydroxymethylacenaphthene <u>p</u> -toluenesulfonate	150
Fig. 24	NMR Spectrum of 1,1,3- or 1,1,2-Trimethylphenalene	151
Fig. 25	IR Spectrum of 2,2-Dimethyl-1-acenaphthenecarboxaldehyde	152
Fig. 26	IR Spectrum of 1,2,2-Trimethyl-1-acenaphthenecarboxaldehyde	152
Fig. 27	IR Spectrum of 1,1,3- or 1,1,2-Trimethylphenalene	152
Fig. 28	NMR Spectrum of 2a,3-Dihydroacenaphthene	151
Fig. 29	NMR Spectrum of 2a,5-Dihydroacenaphthene	151
Fig. 30	UV Spectrum of 2a,3,4,5-Tetrahydroacenaphthene	153
Fig. 31	UV Spectrum of 2a,3-Dihydroacenaphthene	153
Fig. 32	UV Spectrum of 2a,5-Dihydroacenaphthene	153
Fig. 33	NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and One Gram-Equivalent of Potassium (with Olefinic Products)	154



- Fig. 34 NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and One Gram-Equivalent of Potassium (no Olefinic Products) 154
- Fig. 35 NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and 2.1 Gram-Equivalents of Potassium at Room Temperature 154
- Fig. 36 NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and Two Gram-Equivalents of Lithium 155
- Fig. 37 NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and One Gram-Equivalent of Potassium, Followed by Methylation 155
- Fig. 38 NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and Two Gram-Equivalents of Potassium, Followed by Methylation 155
- Fig. 39 NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and One Gram-Equivalent of Lithium, Followed by Methylation 156
- Fig. 40 NMR Spectrum of the Products Obtained from the Metalation Reaction Between Acenaphthene and Two Gram-Equivalents of Lithium, Followed by Methylation 156



## INTRODUCTION

### A. The Problem.

Although the chemistry of indene, including various metalation reactions, has been investigated extensively, very little is known about the direct metalation of indene and its 1- and 3- substituted derivatives by alkali metals. Accordingly work was begun which might aid in the understanding of these reactions.

Interest in the problem developed as a result of a detailed study concerning the metalation and alkylation of a similar benzocyclopentadiene, fluorene. In order to gain more information concerning the behavior of alkali metals towards "acidic" hydrocarbons, it was thought to extend the work on fluorene to other, but similar systems. By doing so, it was anticipated that a number of problems could be clarified.

First, it was felt necessary to determine the exact pattern of alkylation which can occur in the metalated indene system; i.e. whether monoalkylation results in 1- or 3- substitution. Previous reports in the literature are rather uncertain and questionable.

Secondly, the problem of mono- versus polyalkylation using one or two equivalents of metal could be studied, since even trisubstituted derivatives are possible in the indene molecule. At the same time, the question as to whether dialkylation results in 1,1- or 1,3- disubstituted indenenes could be answered.



Elucidation of the reaction mechanism between alkali metals and aromatic systems containing activated methylene units was required, since the evolution of hydrogen gas as opposed to the reduction of double bonds has been the subject of dispute in recent years.

Fourth and finally, it was hoped that this work would eventually lead to the development of convenient synthetic routes whereby alkylated indenenes could be prepared.

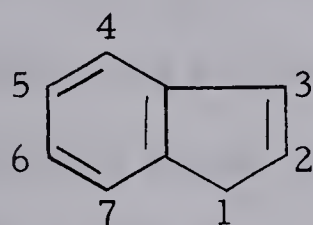
For exactly similar reasons, the metalation of acenaphthene was undertaken. Very little work of this nature has been carried out on this molecule, no doubt due to the poorly activated methylene group present in acenaphthene. Of particular interest was the synthetic aspect of the problem, since substituents on the five-membered ring of acenaphthene are very difficult to insert by direct routes. It was thus hoped that alkyl groups could be introduced via the metalation reaction. To assist in the study of these problems, the preparation of C<sub>1</sub>- and C<sub>2</sub>-substituted acenaphthenes was undertaken by means of conventional synthetic pathways.

#### B. Literature Survey.

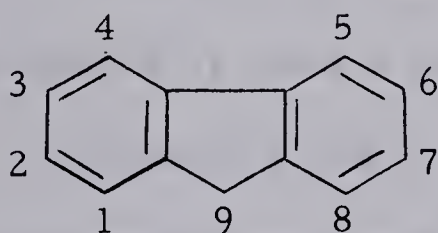
Alkylation reactions of organic compounds with a variety of basic reagents have been examined as early as the nineteenth century, and continue to be under investigation up to the present time. As a result, a vast amount of data has been accumulated on this subject, with the major



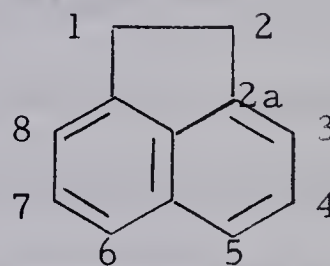
portion of the work on alkylation having been carried out on methylene ( $\text{CH}_2$ ) or methynyl ( $\text{CH}$ ) groups activated by electron-withdrawing functional groups such as carbonyl, carboalkoxyl, nitro, nitrile, halogen etc. . Hydrocarbons themselves, however, in which a methylene unit is activated by one or more aromatic rings, and/or by the presence of other double bonds, have also received considerable attention. Well-known examples in this group include cyclopentadiene and the benzocyclopentadienes, indene(I) and fluorene (II). Although of a somewhat different nature than compounds I and II, acenaphthene (III) is also included\*.



I



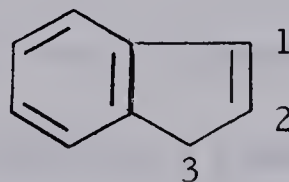
II



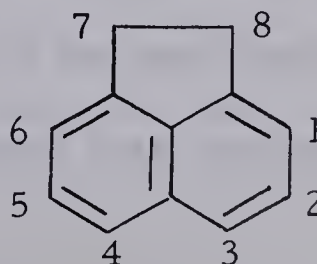
III

---

\*Note: The numbering sequence used in this work follows that used by Chemical Abstracts and is indicated in the above structural formulae. Considerable confusion exists in the literature due to usage of a different system. In many cases, Beilstein included, indene is numbered as follows:



By numbering  $\text{C}_1$  as  $\text{C}_3$ , the problem involving double bond isomerism has been greatly compounded. Similarly, acenaphthene has in many instances been numbered in the following manner, starting with the aromatic rings:





## 1. The Indene System.

Although Baeyer and Perkin Jr. (1) were actually the first to work with the  $C_9H_8$  hydrocarbon indene, named indonaphthene at that time, Krämer and Spilker (2) are often given the credit for formulating the indene molecule in 1890. Five years later, Marckwald (3) pointed out the weakly acidic character of indene, by comparing it with the reduced basicity of the indole molecule. Although alkylated indenenes were not obtained from the reaction of indene with sodium alcoholate and alkyl halides, condensations with benzaldehyde and amyl nitrite were successful at that time. From then on, the 1-metalated derivative of this pseudo-acid has been prepared by using a variety of basic reagents, formation of the "salt" undoubtedly aided by the fact that the indenyl anion is isoelectronic with naphthalene, and thus possesses the stability characteristic of aromatic systems.

### (i) Acidity of Indene.

Due to the acidic nature of the molecule, various attempts have been made to establish a definitive  $pK_a$  value for indene. The work often cited is that by Conant and Wheland (4), who attempted to obtain acidity values for hydrocarbons by studying competitive equilibria of the type



where M is the metal. The reactions were followed either by colorimetric comparisons of the salts, or by carbonation of the equilibrium mixture.

The authors assumed however, that carbonation was complete and faster

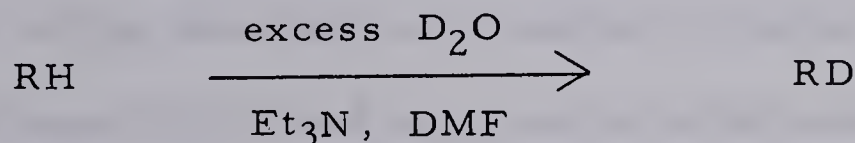


than cross-metalation, an assumption open to question since equilibrium shifts may be more rapid than carbonation (5). The relative amounts of the isolated carboxylic acids were taken as diagnostic for the position of the equilibrium in the metalation reaction. By basing the scale upon the  $pK_a$  value of acetophenone ( $pK_a = 20$ ) and the slightly stronger "acid" ethyl alcohol ( $K = 7 \times 10^{-20}$ ) the following assignments were made:

phenylacetylene, indene, 9-phenylfluorene	$pK_a = 22$
fluorene	$= 24$
etc.	

Using colorimetric, spectroscopic and polarimetric methods to evaluate the intermetalation equilibria in benzene, McEwen (6) extended this work to include other hydrocarbons, and as well alcohols and amines. Based upon methyl alcohol ( $pK_a = 16$ ), indene was assigned a value of 21, fluorene 25, triphenylmethane 33, diphenylmethane 35, and cumene 37, an order which appears reasonable on theoretical grounds.

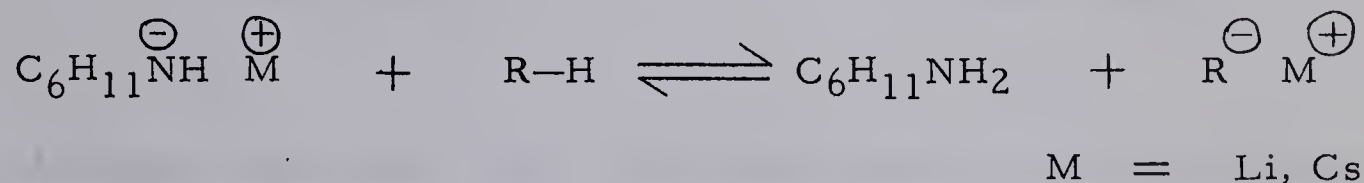
Dessy (5) has questioned some of this work however, and has reinvestigated it by spectrophotometrically (infrared) measuring the rate of proton exchange with deuterium oxide in homogeneous media:



Streitwieser Jr. (7) also felt that the McEwen scale was incorrect, since it was seriously compressed for  $pK_a$  values above 20. By using Hückel's Molecular Orbital (HMO) method, Streitwieser devised a tentative



scale of acidities, in which indene was assigned a  $pK_a$  value of 23, fluorene 31, toluene 59. At a later date, however, the same author (8) realized that his criticisms could not be sustained, and that a serious deficiency existed in the molecular orbital argument. From further equilibrium studies according to the reaction



and using visible spectra of the solutions, a new scale was set up, based upon 9-phenylfluorene having a  $pK_a$  value of 18.5. Although indene was not included in this study, it would seem to have a similar value.

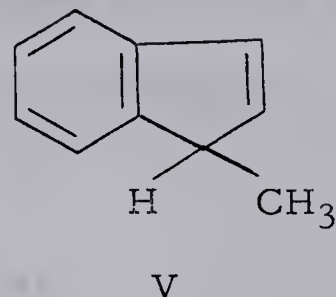
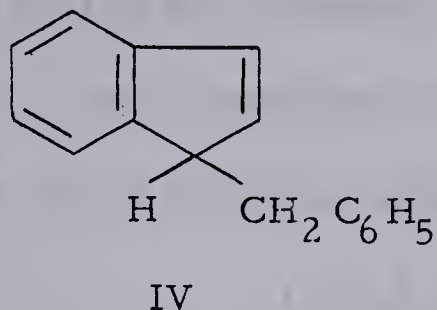
Additional data were obtained by Steiner and Gilbert (9) by spectrophotometrically measuring the conversion of "acids" into their anions in dimethyl sulfoxide (DMSO) solutions. By this method the  $pK_a$  value of indene was found to be 18.2. Highly dissociated ions, rather than ion pairs may be involved due to the high dielectric constant of the solvent. If this interpretation is correct, applications of  $pK_a$  scales will require cognizance of the ionic state, and the solvent system used.

(ii) Metalations and Subsequent Reactions.

After finding alkoxides to be ineffective bases for the metalation of indene, Marckwald (10) turned to the use of solid metal hydroxides. By heating equal parts of indene and benzyl chloride with excess powdered potassium hydroxide for 6 hours at  $160^{\circ}$ , he isolated a product supposedly benzylated in the 1-(or  $\alpha$ ) position (IV). Similarly, when benzyl chloride



was replaced by methyl iodide, 1-methylindene (V) was proposed as the structure of the product obtained.



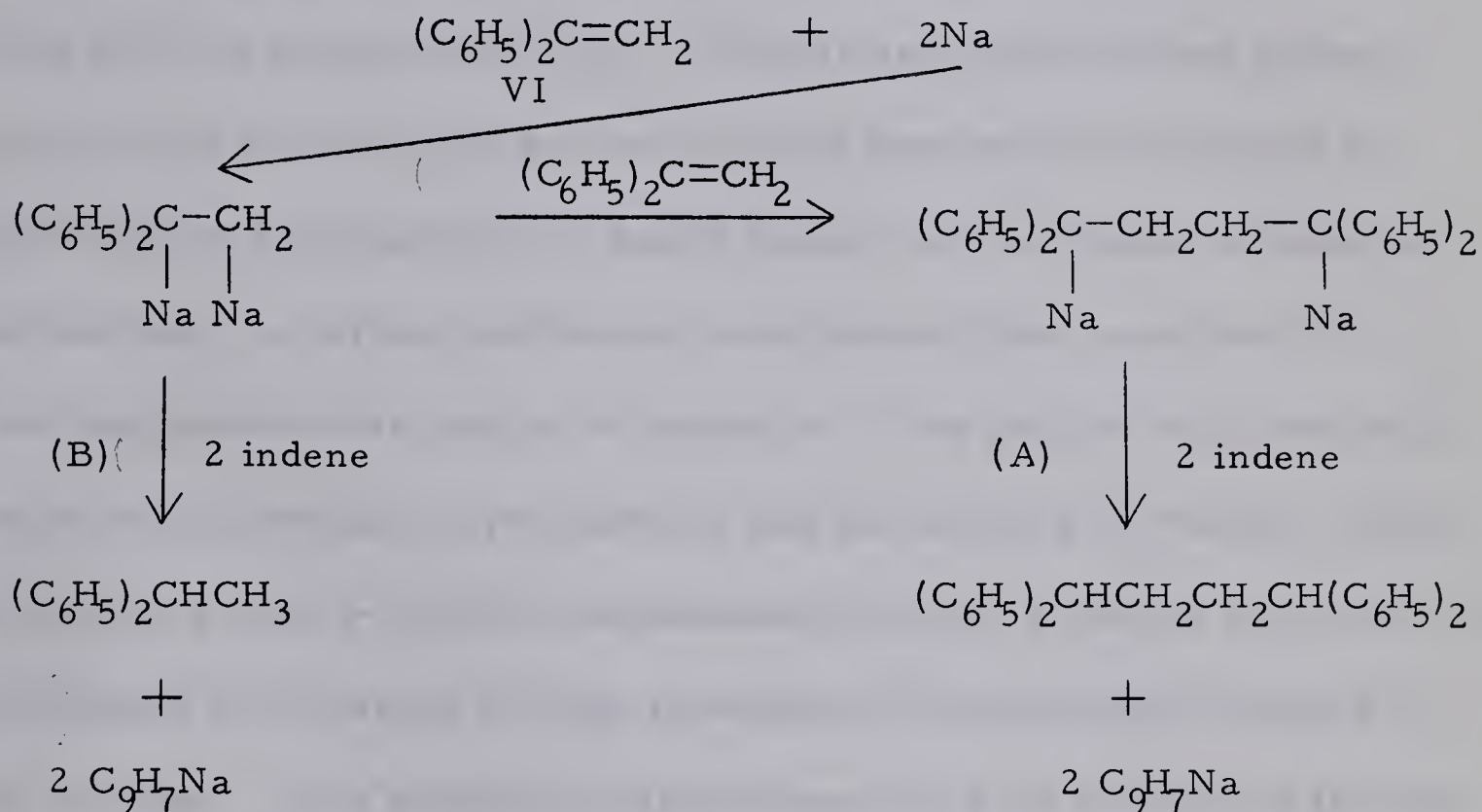
Although in the past alkali metal hydroxides have been used only occasionally as the base in such reactions, their utility has been demonstrated quite recently (11). In fact catalytic quantities of potassium hydroxide or sodium hydroxide were sufficient to bring about the alkylation of indene and fluorene with alcohols and diols at temperatures ranging up to  $250^{\circ}$ .

In order to obtain pure indene from coal-tar fractions, Weissgerber (12) found sodium amide to be an effective reagent. Along with evolved ammonia, 1-indenylsodium could be readily obtained by heating a mixture of indene and sodium amide for 2 hours at  $110-115^{\circ}$ . The same sodium salt could be prepared by employing sodium metal at somewhat higher temperatures ( $140-150^{\circ}$ ), and extended reaction periods. The addition of approximately 2% of organic bases (aniline, toluidine, and particularly pyridine) to the starting material made it possible to obtain the desired product within 3 hours at  $100-105^{\circ}$ . Similar findings of this nature have been reported by Walters (13).

The use of another organosodium compound to generate the



1-indenylsodium is reported by Ziegler and Schäfer (14). The addition of two moles of sodium to an ethereal solution of one mole of 1,1-diphenylethylene (VI) in the presence of two moles of indene led to the desired product. Two competing reactions, A and B, were thought to take place as shown in the following equation.



Eighty per cent or more of the product formed by way of the faster route B. Since route B involved reduction of the ethylenic double bond, the authors investigated the possible generation of "nascent" hydrogen from the reaction between sodium and indene. By comparing the reaction rates of sodium with 1,1-diphenylethylene, sodium with indene, and sodium with a mixture of the two hydrocarbons, the conclusion was reached that the first-mentioned reaction was much faster than the second. Very little sodium was consumed by the indene itself under the experimental conditions (ether solution, 3-4 hours shaking).

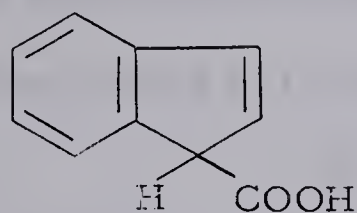


In an investigation of the preparation of a sodium derivative of indene, Lebeau and Picon (15) described the action of sodium on indene in liquid ammonia in an autoclave at ordinary temperatures. They reported that subsequent evaporation of the ammonia and extraction of the residue with petroleum ether gave a 50% yield of the reduction product, indan, along with the sodium derivative. Similar reactions between diphenylmethane and fluorene with sodium in liquid ammonia also resulted in simultaneous hydrogenation of double bonds, with formation of disodium derivatives. A tetrahydrofluorene was obtained after reaction of dimethylfluorene with sodium in ammonia. The authors thus found that saturated and ethylenic hydrocarbons were not attacked by  $\text{Na}/\text{NH}_3$ , while acetylenic groups ( $-\text{C}\equiv\text{CH}$ ) simultaneously formed a sodium derivative and a saturated hydrocarbon through reduction by the hydrogen liberated in the reaction. The aromatic hydrocarbons were not attacked in the ring, but an ethylenic group in the sidechain was hydrogenated. Polycyclic hydrocarbons were variously attacked with ring fission, hydrogenation, and sometimes with formation of sodium derivatives.

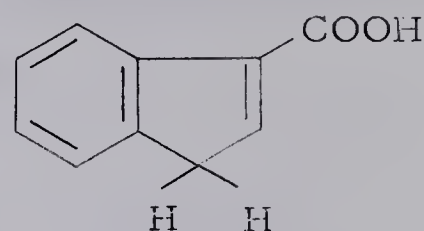
In 1960, a paper by Normant and Angelo (16) described the use of a naphthalene-sodium system in tetrahydrofuran (THF) to metalate indene and other acidic hydrocarbons. Reaction between the naphthalene radical-anion and indene resulted in 1-indenylsodium in addition to a mixture of naphthalene and dihydronaphthalene. On carbonation, however, the yield of indene-1-carboxylic acid (VII) was only 44%. The structure of this



acid is questionable, as a recent communication (17) indicated that indene-3-carboxylic acid (VIII) is formed, rather than VII.



VII



VIII

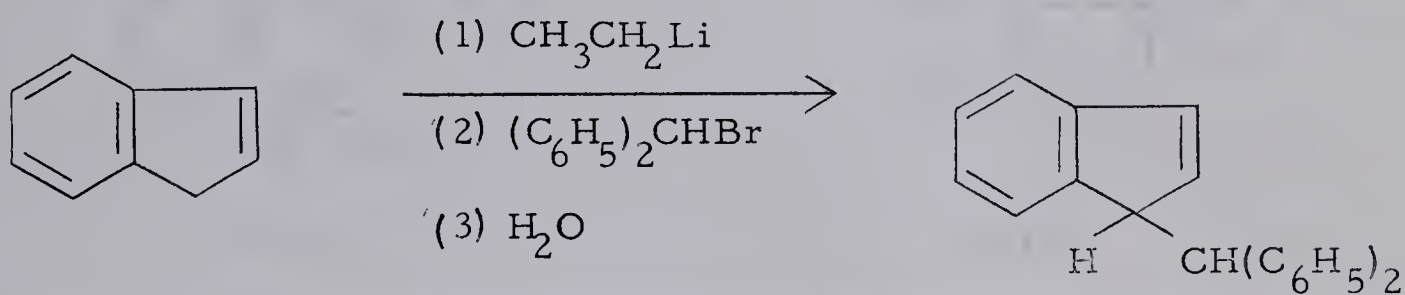
The use of Grignard reagents to remove a hydrogen atom from the indene molecule was first reported by Grignard and Courtot (18). Experimental details, reported in a later paper (19) show that 1-indenyl-magnesium bromide is obtained by heating indene with ethylmagnesium bromide for 10 hours in toluene at 100°. It separates in large crystals, from which a number of 1-substituted indenenes can be prepared. Zerewitinoff (20) used the same reaction for the quantitative determination of active hydrogen in organic compounds. Although indene and fluorene did not react with methylmagnesium iodide in pyridine solution at room temperature, a quantitative reaction with one hydrogen atom occurred at 85°, with evolution of one mole-equivalent of methane gas.

Furthermore, the action of indene on a series of aliphatic organomagnesium derivatives (RMgX) at 40-50° in di-n-butyl ether has been used to measure the rate of hydrocarbon (RH) evolution, in order to determine the bond forces between R and MgX (21).

The use of organolithium compounds as strong bases is reported in detail by O. Blum-Bergmann (22) and also by Schlenk and Bergmann (23).

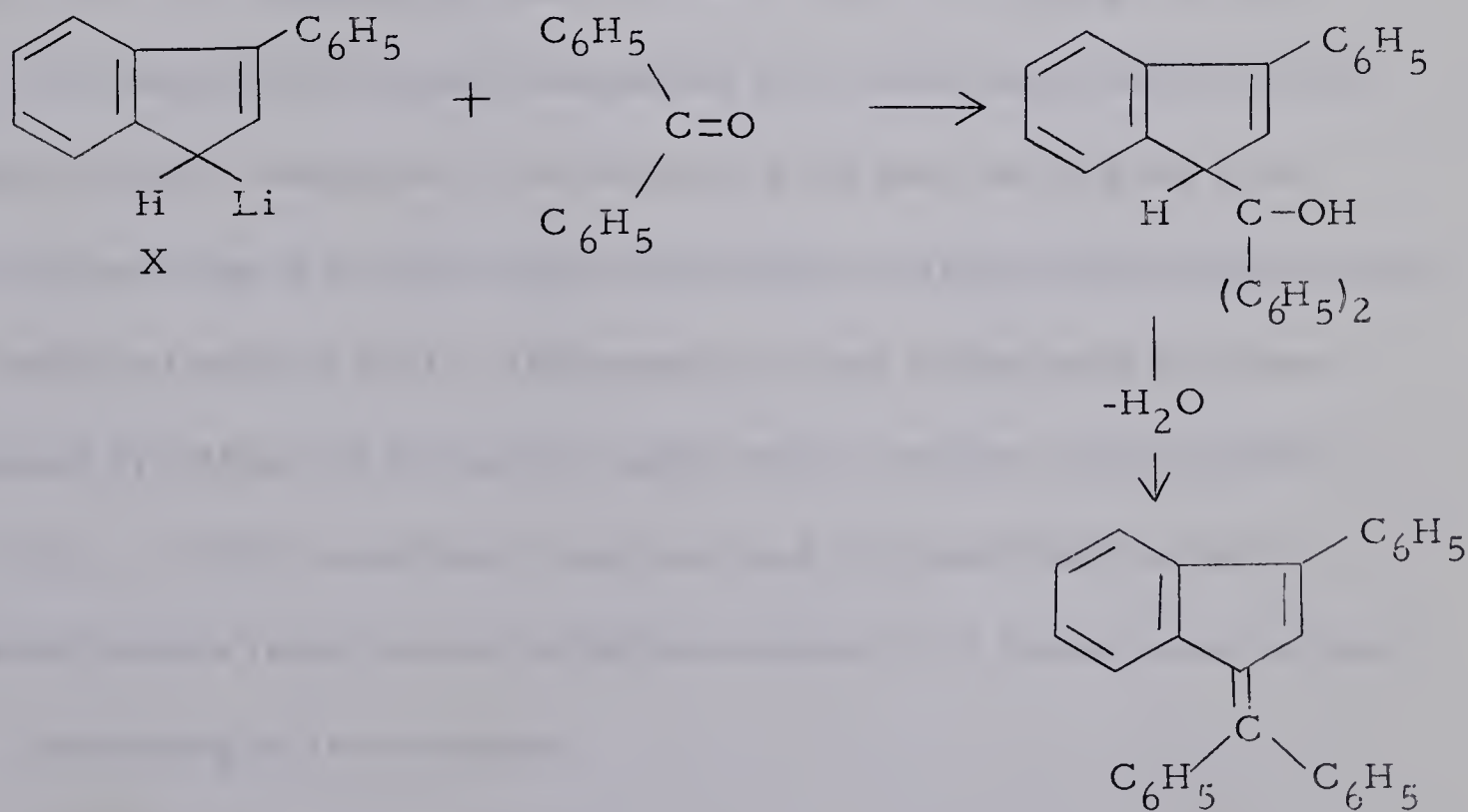


From the reaction between diethylmercury and lithium metal, a benzene solution of ethyllithium was obtained. This was treated with indene, followed by diphenylbromomethane, and gave 1-benzhydrylindene (IX) in good yield according to the following reaction.



IX

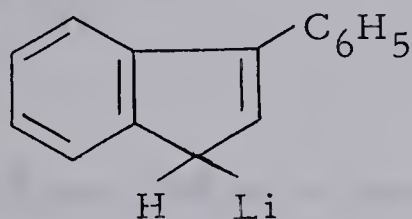
Even after careful work-up, none of the isomeric 3-benzhydrylindene was found. Similarly, from the reaction of 3-phenyl-1-indenyllithium (X) with benzophenone, followed by dehydration of the product, 1-benzhydrylidene-3-phenylindene (XI) was obtained.



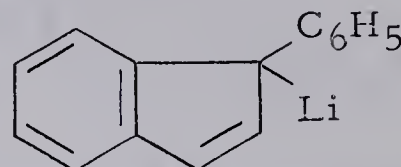
XI



This then established the structure of the organolithium compound as the 1-lithio-3-phenyl derivative (X), and not as the allylic isomer, 1-lithium-1-phenylindene (XII).

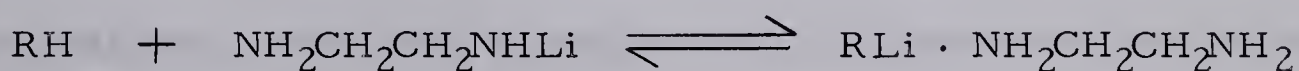


X



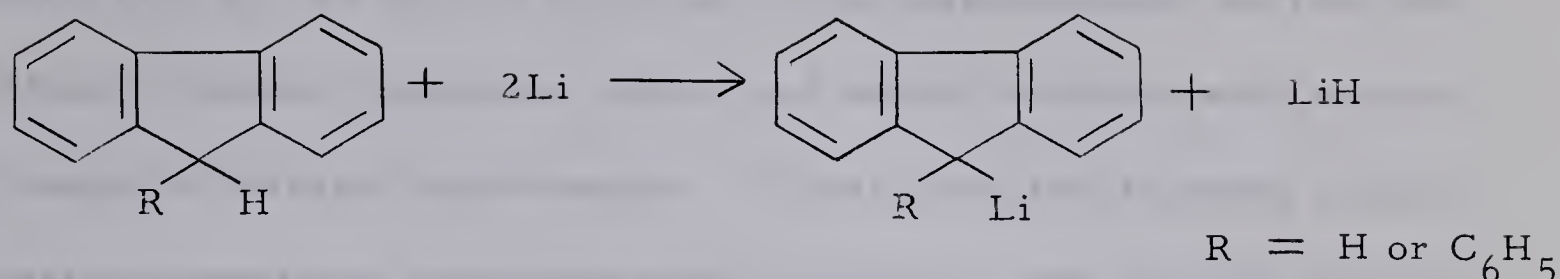
XII

n-Propyllithium has also been used as the metalating agent (24) as have lithiated diamines (25). Etheral solutions of N-lithioethylene-diamine react smoothly with indene and other hydrocarbons at  $-10^{\circ}$  or at room temperature. In general the product isolated (85-95% yield) is a 1:1 crystalline solid complex of the lithiated derivative with ethylene-diamine, according to the following equation.



Although alkyllithium compounds have been used extensively in organometallic reactions, it is not until 1958 that we find the first reported example of an aromatic hydrocarbon reacting with lithium metal in an ethereal solvent (26). (Phenanthrene and anthracene had been metalated by lithium at an earlier date, but no solvent was specified (22, 23)). In THF as solvent, fluorene and 9-phenylfluorene were metalated with a large excess of lithium metal at or below room temperature, according to the equation:





yielding 72% and 38% of 9-fluorenenecarboxylic acid and 9-phenylfluorene-carboxylic acid respectively after carbonation. Likewise, cyclopentadiene reacted with lithium metal to give a 45% yield of diphenylfulvene after treatment of the reaction mixture with benzophenone. A gas, presumably hydrogen, was also evolved during the reaction.

Repetition of this work, as well as a detailed study of the chemistry of alkali metal-unsaturated hydrocarbon adducts (27) revealed different results. The 1:1 adduct of lithium metal and biphenyl in THF solution as a metalating agent toward pseudo acidic hydrocarbons was found to be an excellent substance for the synthesis of certain organolithium compounds. In addition, new insight was gained as to the mechanism of such metalations, and in the metalations carried out by Gilman (26). In fact the above equation was shown to be incorrect, and as such a new mechanism was proposed. Results along similar lines were published nearly the same time by House and Kramar (28). Their work will be discussed later in the appropriate section for Results and Discussion. (p.46-47).

The work which led to our study of the indene and acenaphthene series was the metalation and alkylation of fluorene (29), published in a

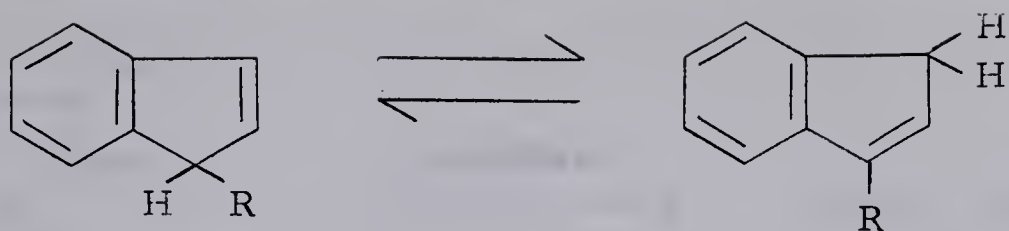


series of papers (30). In this work, the metalation of fluorene by alkali metals (Li, Na, K) and the reactions of the organometallic derivatives with alkyl halides, deuterium oxide, and benzoyl chloride were studied by means of infrared spectroscopy. It was found that fluorene could be metalated readily by potassium metal in dioxan, THF, and the ethers of ethylene glycol. Dialkyl ethers were inferior, while hydrocarbon solvents were quite inefficient. On the other hand, 9-fluorenyllithium and -sodium could only be prepared successfully in THF or in ethers of ethylene glycol. Alkylation or deuteration of these salts, using equimolar quantities, led to mixtures of unchanged starting material, C<sub>9</sub>-mono-, and C<sub>9</sub>-disubstituted fluorene, the yield of the latter being as high as 35% in ether solvents, but less than 10% in hydrocarbon solvents. Disubstitution was found especially in the case of the more reactive potassium and sodium salts, while 9-fluorenyllithium gave little disubstitution in ethereal solvents and produced exclusively monosubstituted fluorene in hydrocarbon solvents. The results of this work were explained in terms of a) solubilities of the organometallic compound b) participation of the ether solvents in the metalation reaction c) polarity of the carbon-metal bond and d) acidity of the hydrocarbon and the monosubstituted hydrocarbon.

(iii) Isomerization in the Indene Ring System

Due to tautomerism in the five-membered ring, two structures are possible for monosubstituted indenenes:



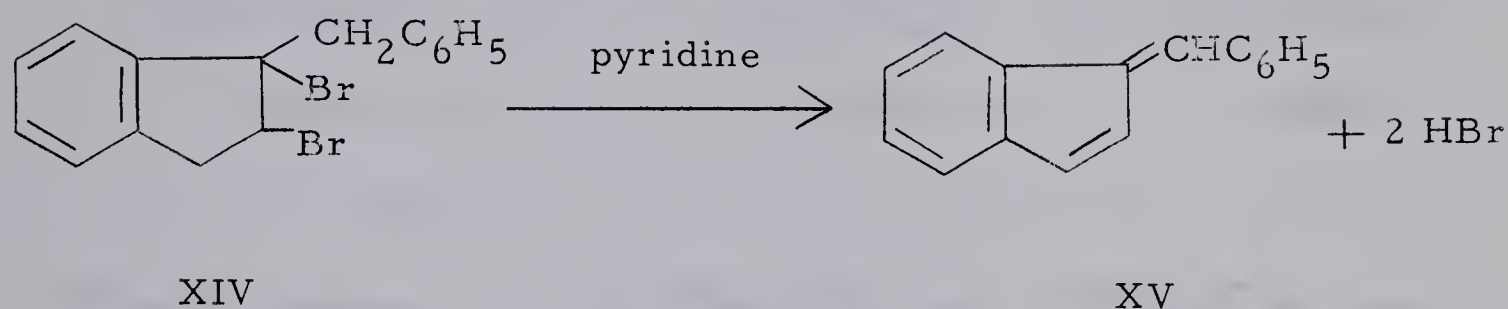
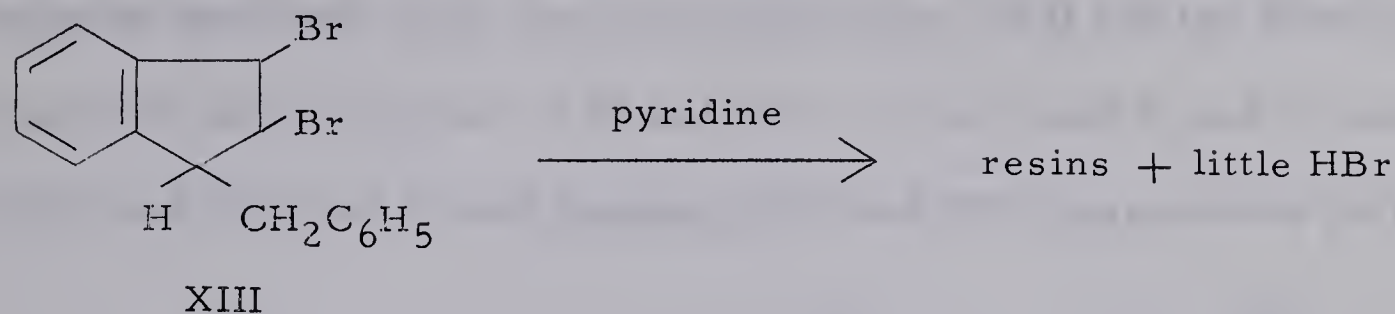


There has, however, been much discussion in the literature as to whether these two tautomeric compounds can exist separately. As mentioned earlier, Marckwald (10) reported the formation of 1-benzyl- and 1-methylindene from the reaction of indene with the appropriate alkyl halide in the presence of potassium hydroxide at 160°. Under the same, or similar conditions, Thiele and Bühner (31) claimed to have obtained the 3-(or  $\gamma$ ) isomer. In addition, they concluded that the two isomeric forms were the same, and that isomerization did not exist, due to oscillation of the double bond. Consequently the two described forms of alkyindenenes must be identical.

The work of Courtot (32) however, disproved the "indene oscillation hypothesis". From the reaction of indenylmagnesium halide with benzyl chloride, a liquid benzy lindene was obtained which could be readily converted by alcoholic potassium hydroxide into the solid benzy lindene obtained by Thiele and Bühner. Courtot thus claimed to have obtained 1-benzylindene. He obtained further evidence to support his view from the reaction of the dibromide of this compound. This dibromide (XIII) lost very little HBr on treatment with pyridine, and formed only resins. On the other hand, the dibromide of Thiele's 3-benzylindene (XIV) yielded the known



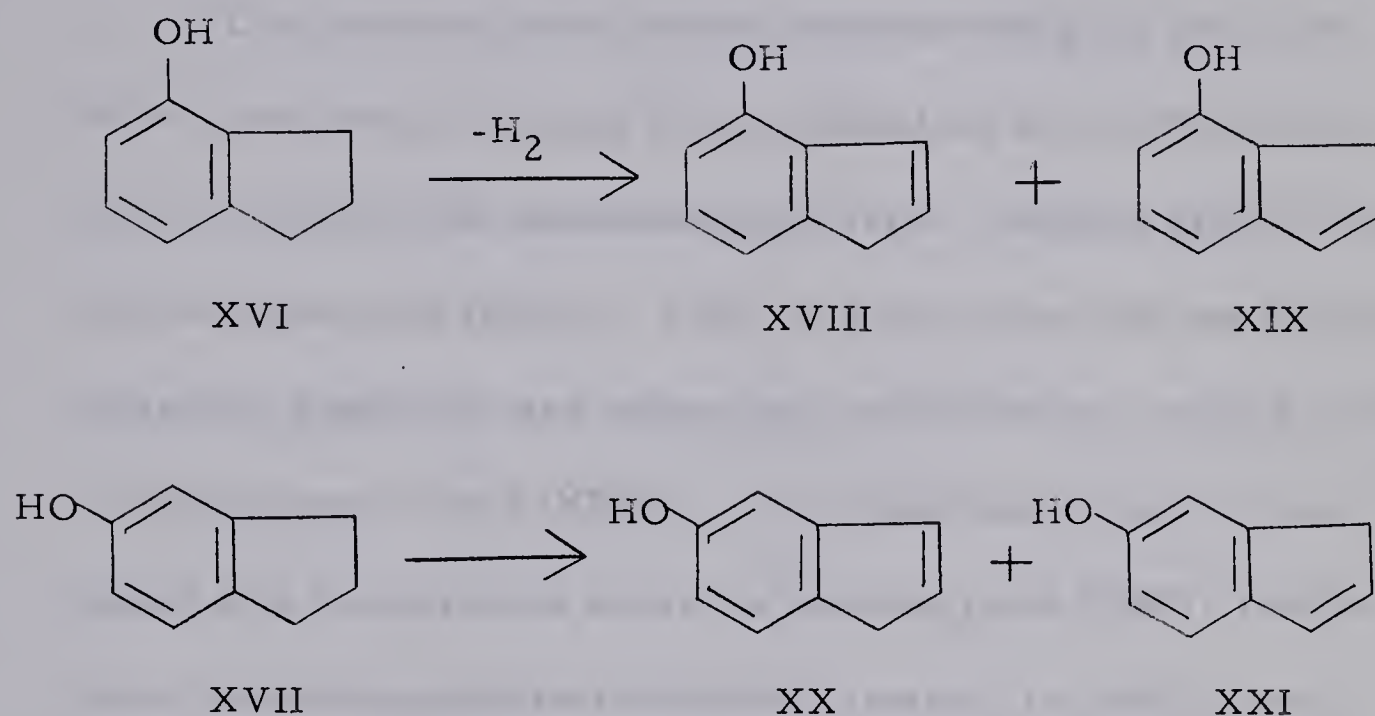
1-benzylideneindene (XV), with spontaneous evolution of HBr.



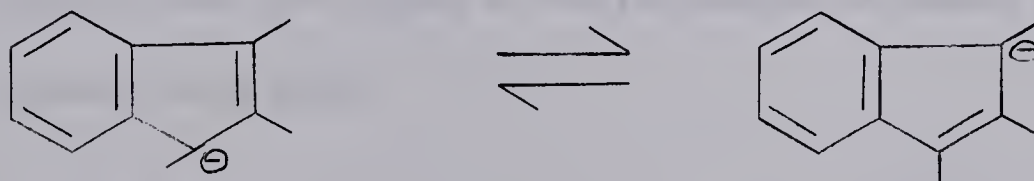
Additional evidence for two distinct isomers was obtained by means of potassium permanganate oxidations (19). The existence of a distinct pair of isomers was finally realized by Thiele himself (33), and was also shown by Wislicenus and Hentrich (34). As result of experiments with 5- and 6-substituted indenenes, Ingold (35) still believed that indene possessed a mobile tautomeric system, an idea which he (36) and also Dewar (37) maintained in spite of contrary evidence (38). If the non-benzenoid double bond could alternate between the 1,2- and 2,3-positions, with a proton oscillating between the 1- and 3-positions, then derivatives containing the same substituent respectively in the 1 and 3, the 4 and 7, and the 5 and 6 positions would be identical. However, as has been shown on many occasions, the double bond is sufficiently static to allow the separate existence of such pairs of isomers. An example of this is seen in the



synthesis of various substituted indenenes (39-41), the most recent work being the synthesis of 5- and 6-methoxyindene (42) and the dehydrogenation of 4- and 5-indanol (XVI and XVII), which yield 4- and 7-indenol (XVIII and XIX) and 5- and 6-indenol (XX and XXI) respectively (43).



Under alkaline conditions, however, the mesomeric anion



is formed, and isomerization occurs very readily between the pairs of compounds. A recent study concerning the kinetics of the isomerization has been reported (41).

#### (iv) Synthesis of the Indene Nucleus.

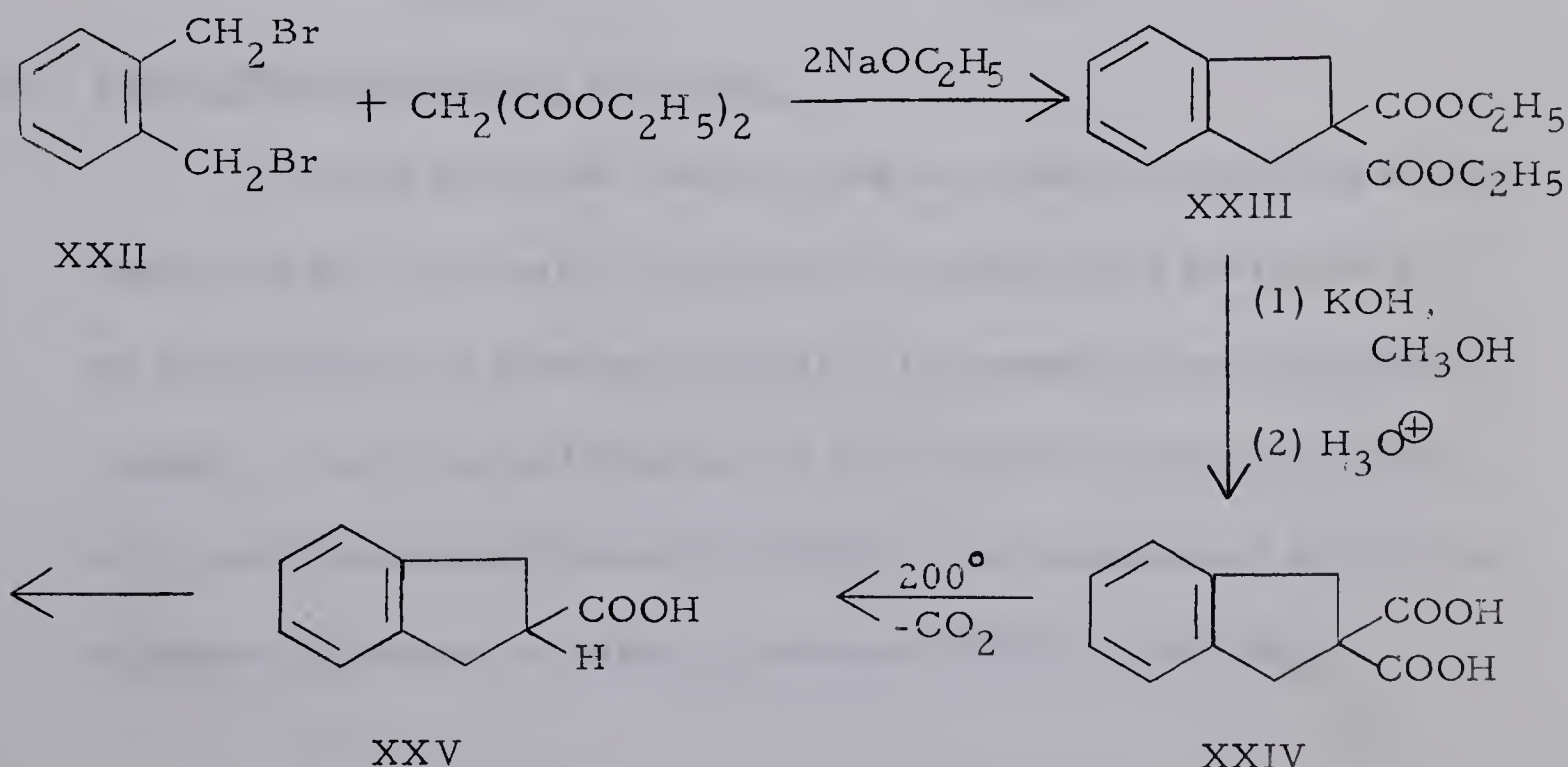
Although the formation of the indene nucleus can be accomplished by various means, only a few reactions are simple and useful enough to be carried out successfully for normal synthetic purposes. For this



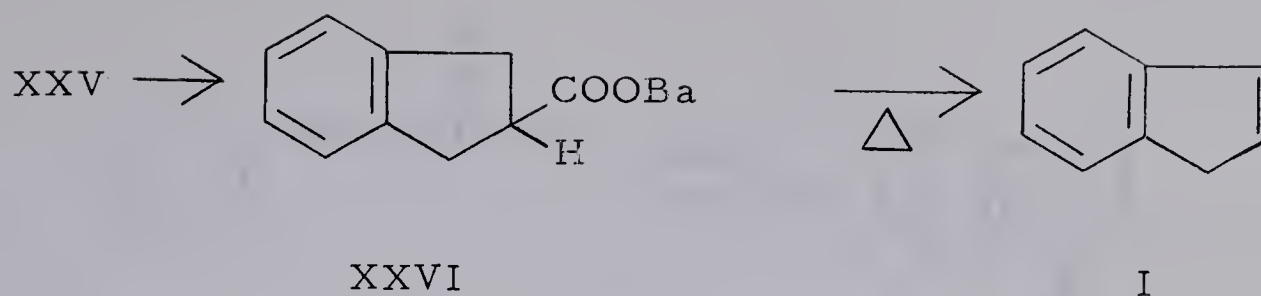
reason, and because of the fact that all the methods of formation have been summarized elsewhere (44a, 45a) only a few of the reactions will be described here.

a. Synthesis from Ortho-Disubstituted Benzenes.

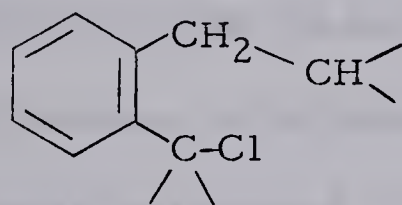
One preparation of indene, demonstrating its structure at the same time, involves the condensation of  $\alpha, \alpha'$ -dibromo-o-xylene (XXII) with diethylmalonic ester, yielding diethyl indan-2,2-dicarboxylate (XXIII). This, on hydrolysis with methanolic potassium hydroxide and subsequent acidification, results in indan-2,2-dicarboxylic acid (XXIV). The dicarboxylic acid, when heated at a temperature above its melting point ( $200^\circ$ ), readily loses one mole equivalent of carbon dioxide, to yield indan-2-carboxylic acid (XXV) (70%). Dry distillation of the barium salt (XXVI) does not result in the formation of indan, but rather of indene itself (46).



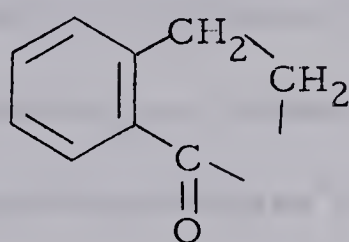




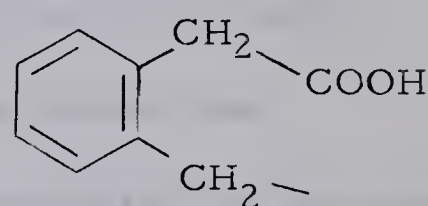
Ring formation is obviously not limited to the above reaction since compounds such as XXVII - XXXI can also be made to undergo either cyclization or condensation leading to the indene ring system.



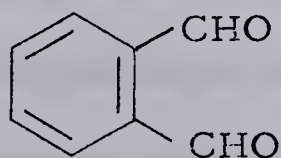
XXVII



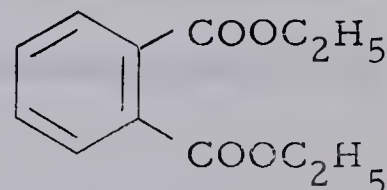
XXVIII



XXIX



XXX

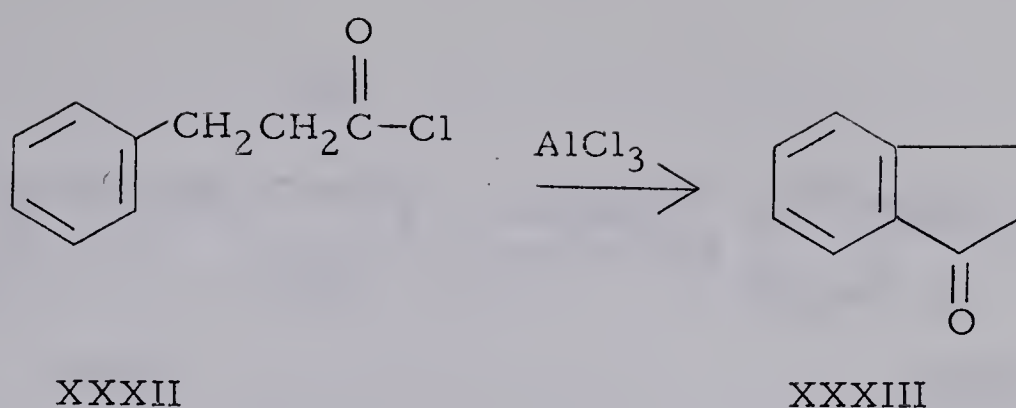


XXXI

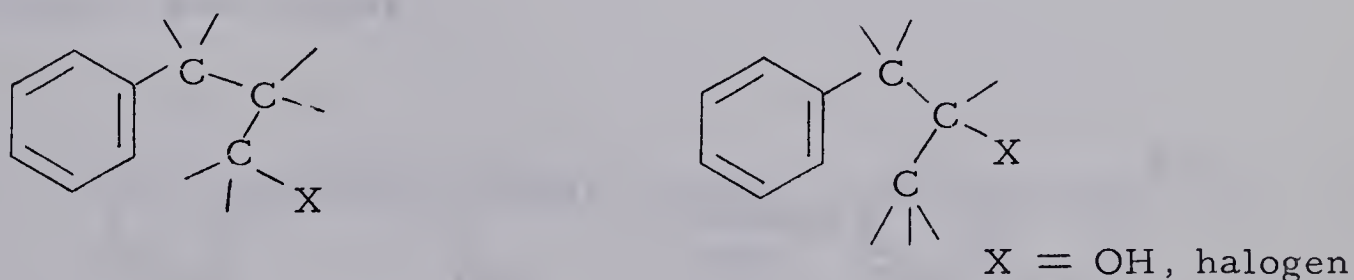
b. From Monosubstituted Benzenes.

Perhaps the most common and most widely used preparative method is the cyclization reaction of cinnamic acid derivatives, or compounds of a similar structure, by means of the appropriate reagent. An excellent example is the Friedel-Crafts cyclization of 3-phenylpropionyl chloride (XXXII) in the presence of anhydrous aluminum chloride, to yield 1-indanone (XXXIII), 90% (47).



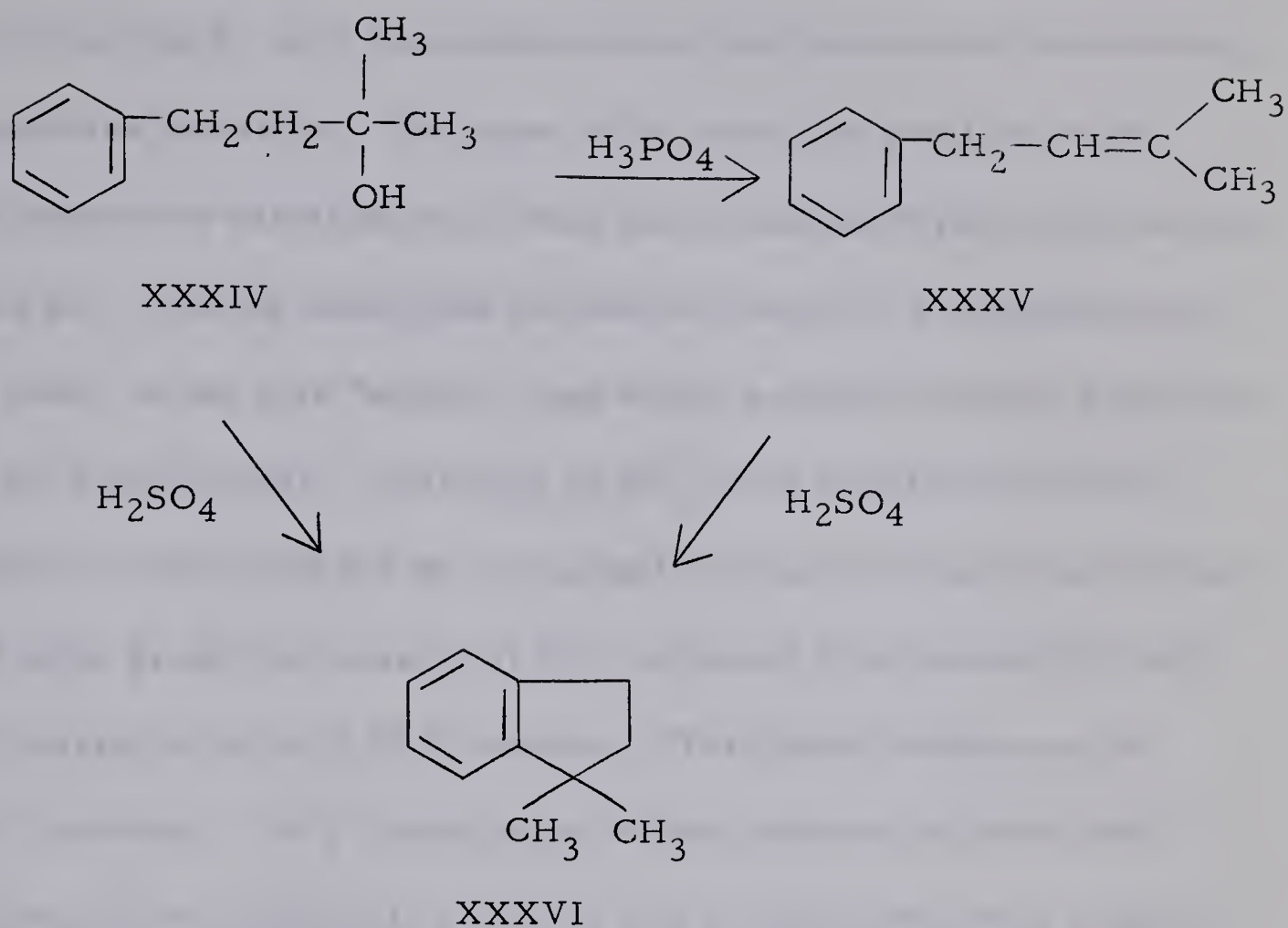


Cyclizations of the corresponding carboxylic acids with hydrogen fluoride and sulfuric acid are also successful, but yields are lower (73% and 27% respectively). If the precursors possess substituents in the appropriate positions either before or after cyclization, substituted indanones, indans, or indenenes can readily be obtained. Similar syntheses are possible from benzene and aliphatic compounds, which in most cases lead at first to hydrocinnamic acid derivatives, which are then cyclized further (48). Cyclodehydrations and cyclodehydrohalogenations of hydroxy or halogen derivatives such as

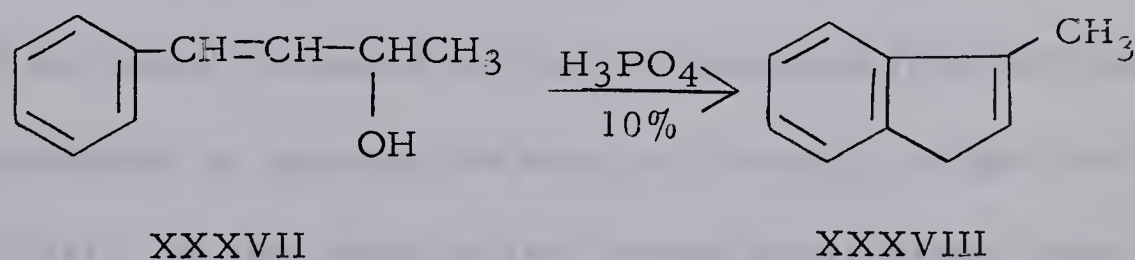


generally proceed via the olefins, which subsequently cyclize, yielding indans. Work along these lines has been published by Bogert and Davidson (49), who cyclized dimethylphenethyl carbinol (XXXIV) to 1,1-dimethylindan (XXXVI).





Campbell and co-workers (50) have studied the dehydration of some phenyl-substituted ethylenic carbinols, and in one case were able to isolate an indene (XXXVIII), although conclusive structural evidence was lacking.



## 2. The Acenaphthene System

### (i) General Nature of the Acenaphthene Molecule, and the Reactivity of the Methylene Groups.



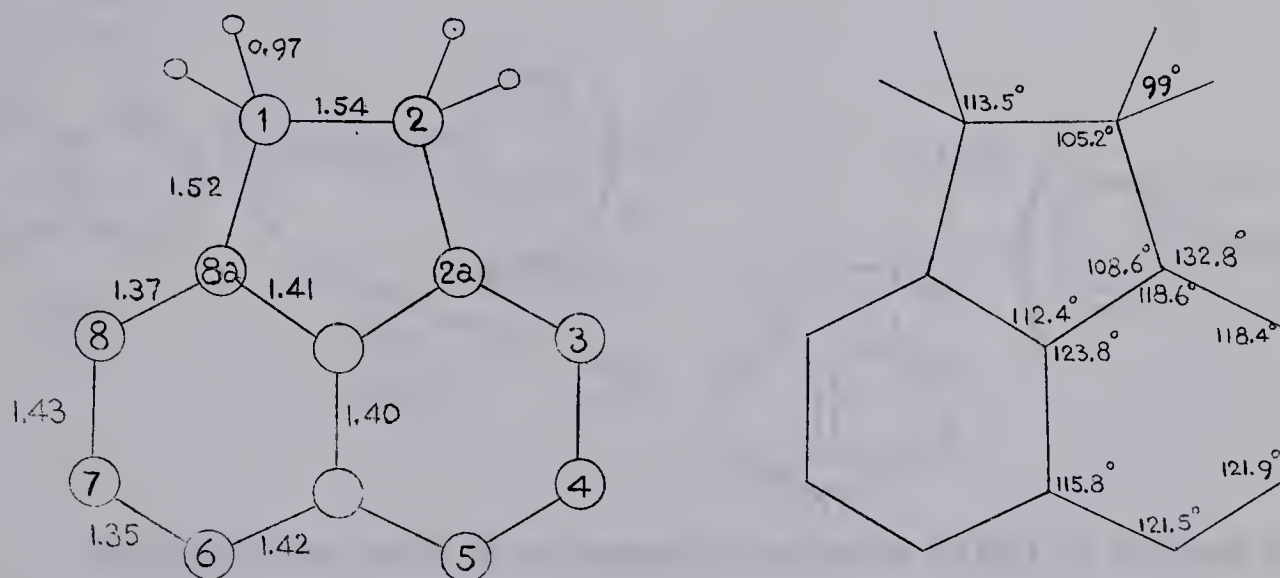
Although the literature abounds with reports dealing with indene pertinent to our work, very little information was encountered concerning the acenaphthene molecule. Because of the favorable position on the  $pK_a$  scale, numerous reactions have been described involving condensations, alkylations etc. with the methylene protons of indene. Acenaphthene on the other hand, is far less "acidic", and would appear to occupy a position far down the acidity scale. Although no  $pK_a$  value could be found for acenaphthene, it may perhaps be comparable to that of toluene and cumene, which are often given the value of 37 (51), although Streitwieser (7) and Cram (52) assign a value of 59 to toluene. This latter value may be incorrect, however. As a consequence of this reduced activity, very few reactions occur selectively at the  $C_1$  and  $C_2$  positions, thus making it difficult to obtain substituents at these positions. Nearly all reactions of acenaphthene reported in the literature therefore involve electrophilic substitution reactions, which occur readily on the aromatic rings (44b, 45b).

The chemistry of acenaphthene can be traced back to at least 1866-67, when Berthelot prepared the parent compound from ethylene and benzene or naphthalene by passing the mixture through a bright red-hot porcelain tube (53). At that time he also heated acenaphthene with potassium metal, from which he obtained a black potassio compound, which on decomposition with water gave back the starting material (54). This observation, which is related to our work, could indicate the intermediacy



of 1-acenaphthenylpotassium.

Being a planar molecule (44b, 45b), acenaphthene seems to possess a certain amount of internal strain in view of the reported values for bond angles and bond distances (55). The most recent X-ray (56) and computational structural analysis (57) indicate, however, that no unusual bond lengths are present, as was formerly believed. The aliphatic  $\text{CH}_2\text{—CH}_2$  bond has a bond length value of  $1.54 \pm 0.02 \text{ \AA}$ , with the steric strain and angular stress being evenly shared among the three fused rings, with  $\angle \text{C}_1\text{C}_2\text{C}_{2a} = 105.2^\circ$  and  $\angle \text{H}_1\text{C}_1\text{C}_2 = 113.5^\circ$ . The bond lengths of the aromatic rings are nearly identical with those for naphthalene. The reported information (56) can be summarized in the following diagrams.

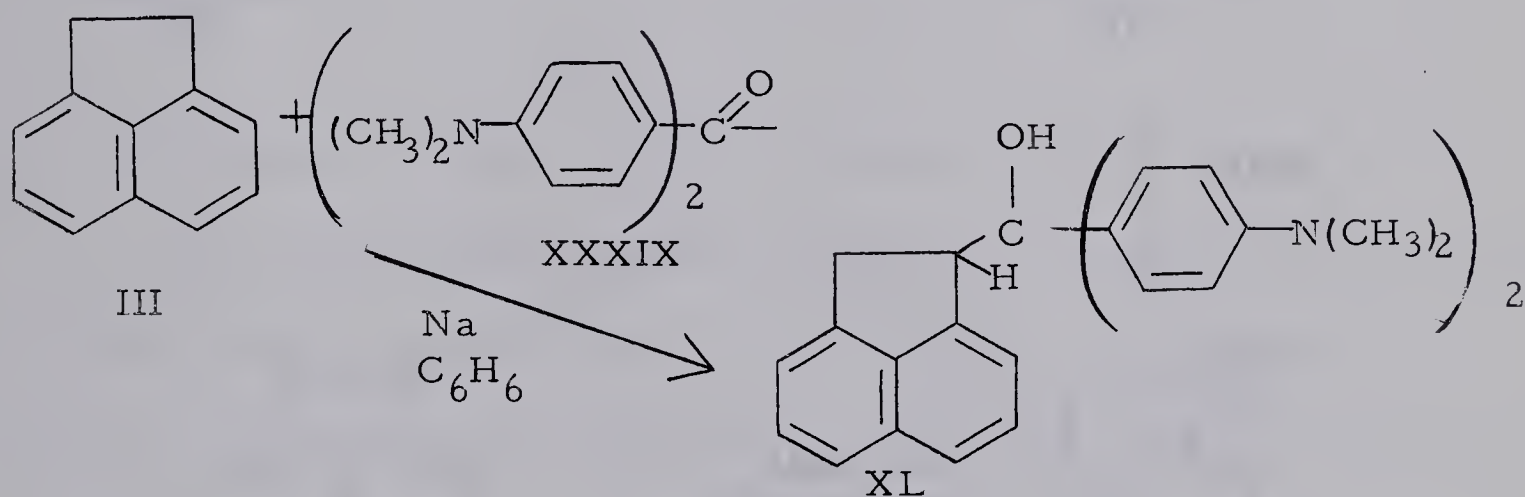


Berliner et al. (58) reported that rates of bromination and solvolysis reactions of acenaphthene and its derivatives were faster than expected, and ascribed this increase in reactivity to the internal strain. Faster rates for lead tetraacetate oxidation of cis and trans-1,2-acenaphthenediols as compared to 1,2-cyclopentane diols and 1,2-cyclohexane diols also seemed to indicate only a minor degree of conformational flexibility (59). In



addition, the cis diol showed very strong intramolecular hydrogen bonding ( $\Delta\nu = 77 \text{ cm}^{-1}$ ), again ascribed to the conformational rigidity of the molecule.

As mentioned previously, very few reactions involving acenaphthene occur at the  $C_1$  and  $C_2$  methylene positions. Reissert (60) reported that the reaction between one mole of acenaphthene and four moles of amyl nitrite in the presence of dry HCl in amyl alcohol afforded a monoxime of acenaphthenequinone in 75% yield. Also the reaction between acenaphthene, Michler's ketone (XXXIX), and sodium in benzene solution was reported to have given bis-(p-dimethylaminophenyl)-1-acenaphthenyl carbinol (XL) (61).

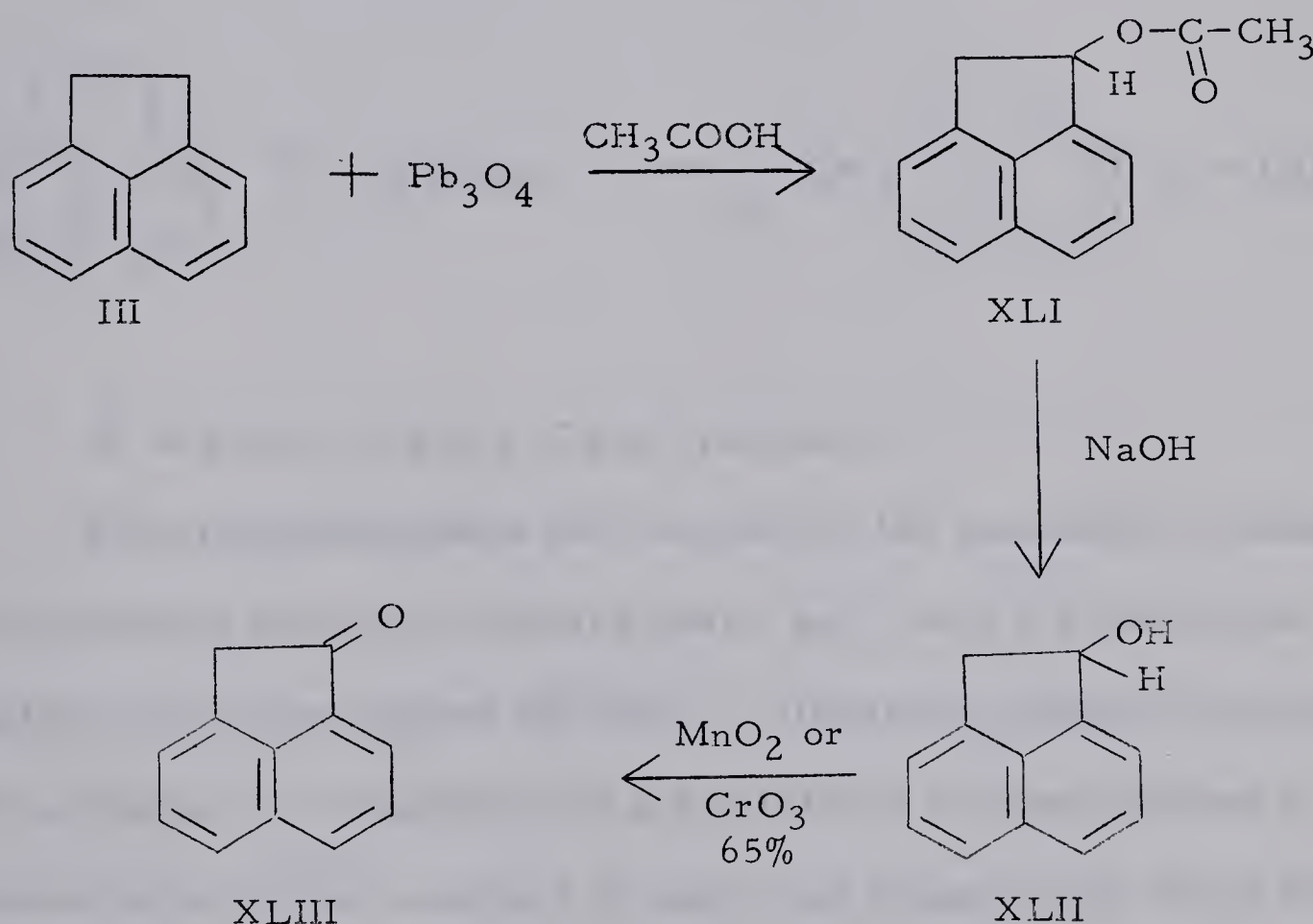


Bromination with N-bromosuccinimide (NBS) in carbon tetrachloride or benzene solution also resulted in substitution at  $C_1$ , yielding 1-bromo-acenaphthene, isolated as 1-acenaphthenyltrimethylammonium bromide (75%). A change to the more polar solvents dimethylformamide (DMF) or propylene carbonate, however, did not produce  $C_1$ -bromination, 5-bromoacenaphthene being the only isolable product (79-94% yield)(62).

The only other reaction taking place at the methylene positions



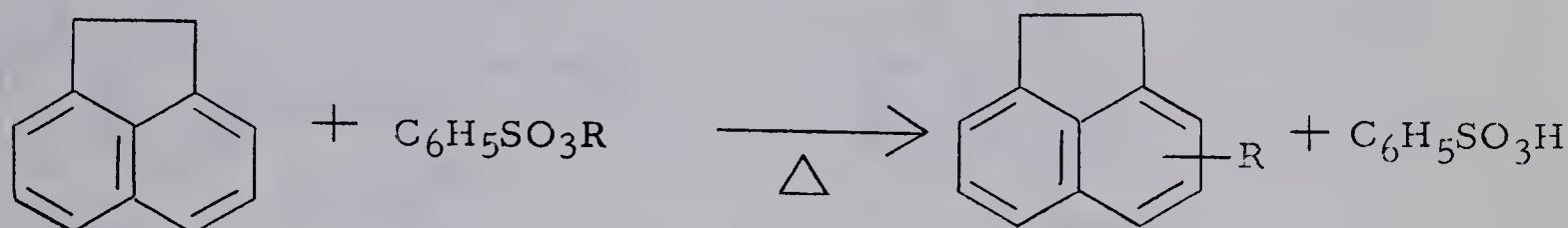
involves oxidations. Even these reactions are of limited value, since strong oxidizing agents such as  $\text{KMnO}_4$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ , etc. yield mainly naphthalic acid (or the anhydride). The only oxidizing agent which does not cleave the  $\text{C}_1\text{—C}_2$  bond is lead tetraacetate. This affords 1-acenaphthényl acetate (XLI), which can be easily hydrolyzed to 1-acenaphthenol (XLII), a compound which can be oxidized to 1-acenaphthenone (XLIII) (63).



Quite obviously, in order to introduce alkyl substituents at the  $\text{C}_1$  and  $\text{C}_2$  positions, it would be necessary to go via the aforementioned hydroxyl, halogen, or carbonyl derivative. However, the dehydro-derivative, acenaphthylene, also offers a number of possibilities.



Virtually all other reactions of acenaphthene give rise to ring substitution, the substituents usually entering the 3- and 5-positions, although 4-acenaphthenyl derivatives are also common. Alkylation of the acenaphthene nucleus has been studied, but the reaction involved the thermal decomposition of alkyl benzenesulfonate esters, in the presence of excess hydrocarbon (64). Mixtures of 3-, 4-, and 5-alkylacenaphthenes were obtained in rather poor yields.

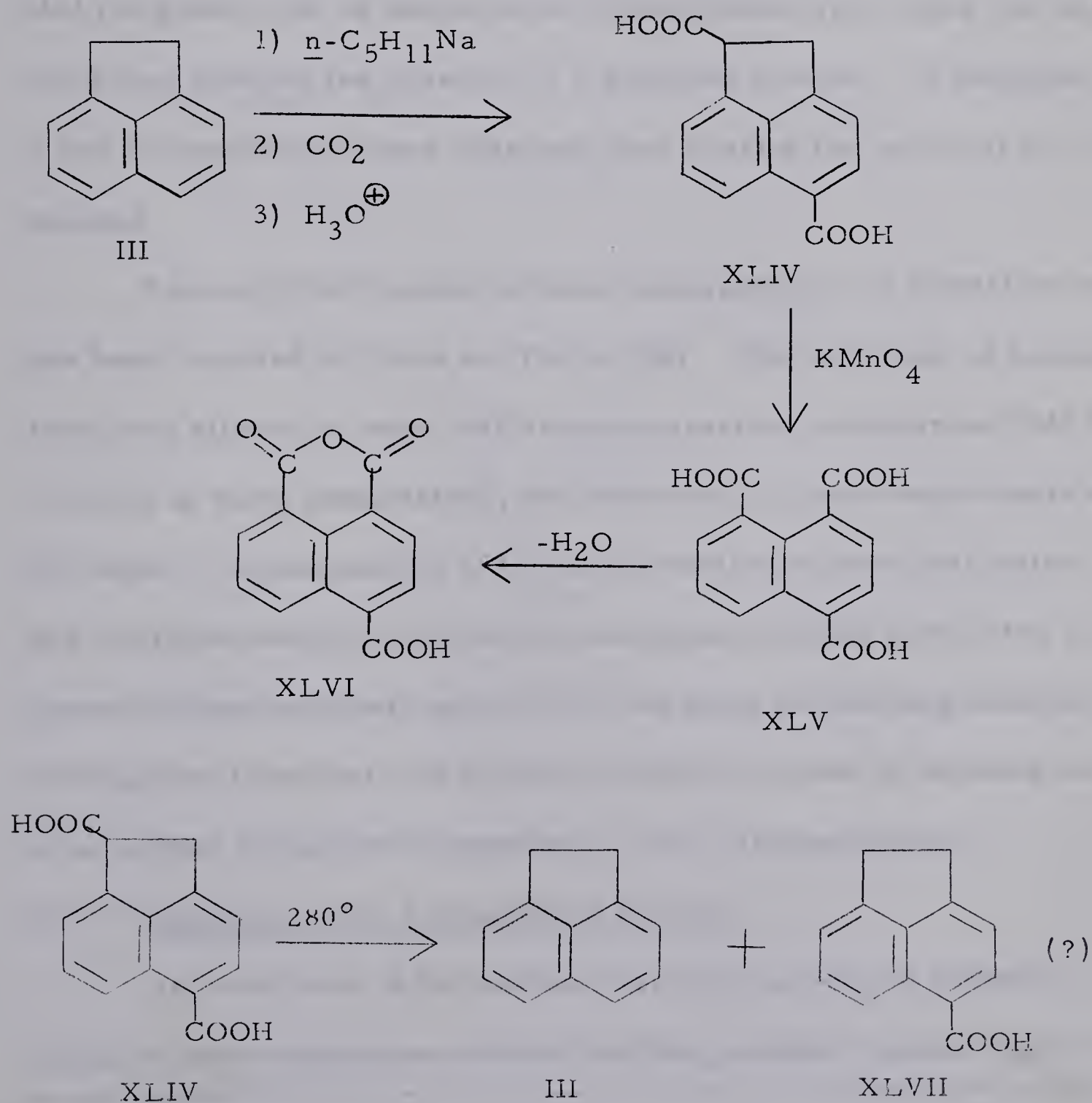


$\text{R} = \text{C}_2\text{H}_5, \text{i-C}_3\text{H}_7, \text{s-C}_4\text{H}_9, \text{cyclohexyl}$

Even though Berthelot (54) carried out the metalation of acenaphthene with potassium nearly one hundred years ago, very few metalation reactions have been carried out since. Gilman and Bebb(65) reported the metalation of acenaphthene by n-butyllithium in ether followed by carbonation, as giving a mixture of mono- and dibasic acids which were not separated. Decarboxylation of the products by heating with calcium oxide and copper gave acenaphthene, while dichromate oxidation yielded naphthalic acid. Morton and co-workers (66) metalated acenaphthene using n-amylsodium in petroleum ether at 30-40°. The results indicated that one sodium atom did, in fact, replace a hydrogen atom in a methylene



group, but a second one entered the ring, giving a dicarboxylic acid upon carbonation in about 50% yield. Although no definite proof was available, the authors felt it was either the 1,6- or, more likely, the 1,5-dicarboxylic acid (XLIV). Permanganate oxidation gave naphthalene-1,4,5-tricarboxylic acid (XLV), indicating that one carboxyl group must have been attached to a methylene unit, while the second was bound to the 5- or 6-position in the aromatic nucleus.





Pudovik and Muratova (67) have metalated acenaphthene using lithium in diethyl ether and methylal. Since their investigation dealt only with the effect of solvent structure on the rate of metalation, no further details concerning reaction products were given, although mention was made of a possible dilithiumdihydroacenaphthene derivative. In diethyl ether, lithium and acenaphthene, when shaken for 40 hours, gave a green-colored solution, which gradually changed to violet. The possibility exists that the green color is indicative of a monolithium salt, while the violet color may indicate the presence of a dilithium species. In methylal, a red-colored solution was observed after shaking the reactants for 20 minutes.

Recently, the reaction between acenaphthene and potassium metal has been reported by Cram and Dalton (68). One millimole of acenaphthene was allowed to react with excess potassium in anhydrous DME\* for 17 hours at room temperature, and consumed 2.1 gram-equivalents of the metal. Decomposition of the black reaction mixture with water, and final analysis by gas-liquid chromatography (GLC) showed two components in approximately equal yield, one being the starting material. Although not identified, the second product was shown by infrared analysis to be neither tetrahydroacenaphthene, nor 1-ethylnaphthalene.

(ii) Synthesis of the Acenaphthene Nucleus.

As in the case of the indenenes, very few successful synthetic routes to the acenaphthene nucleus involving standard organic reactions

---

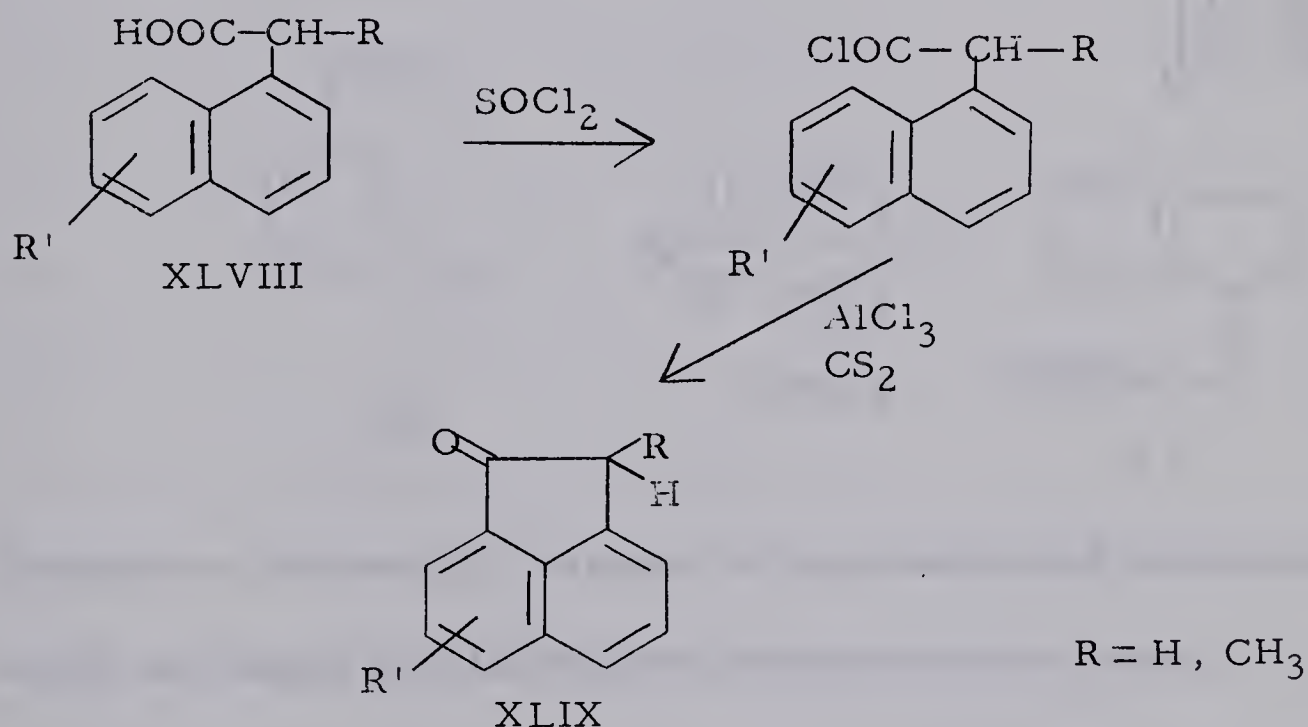
\* 1,2-Dimethoxyethane



exist. For this reason only two pathways will be discussed here.

a. From Naphthalene Derivatives

Perhaps the simplest route to acenaphthenes is by means of the Friedel-Crafts cyclization of the readily available 1-naphthyl-acetic or propionic acids (XLVIII). Even though a strained system is involved, closure of the five-membered ring via the acid chloride-aluminum chloride method takes place remarkably well, with yields of 80-85% being easily obtained (69).



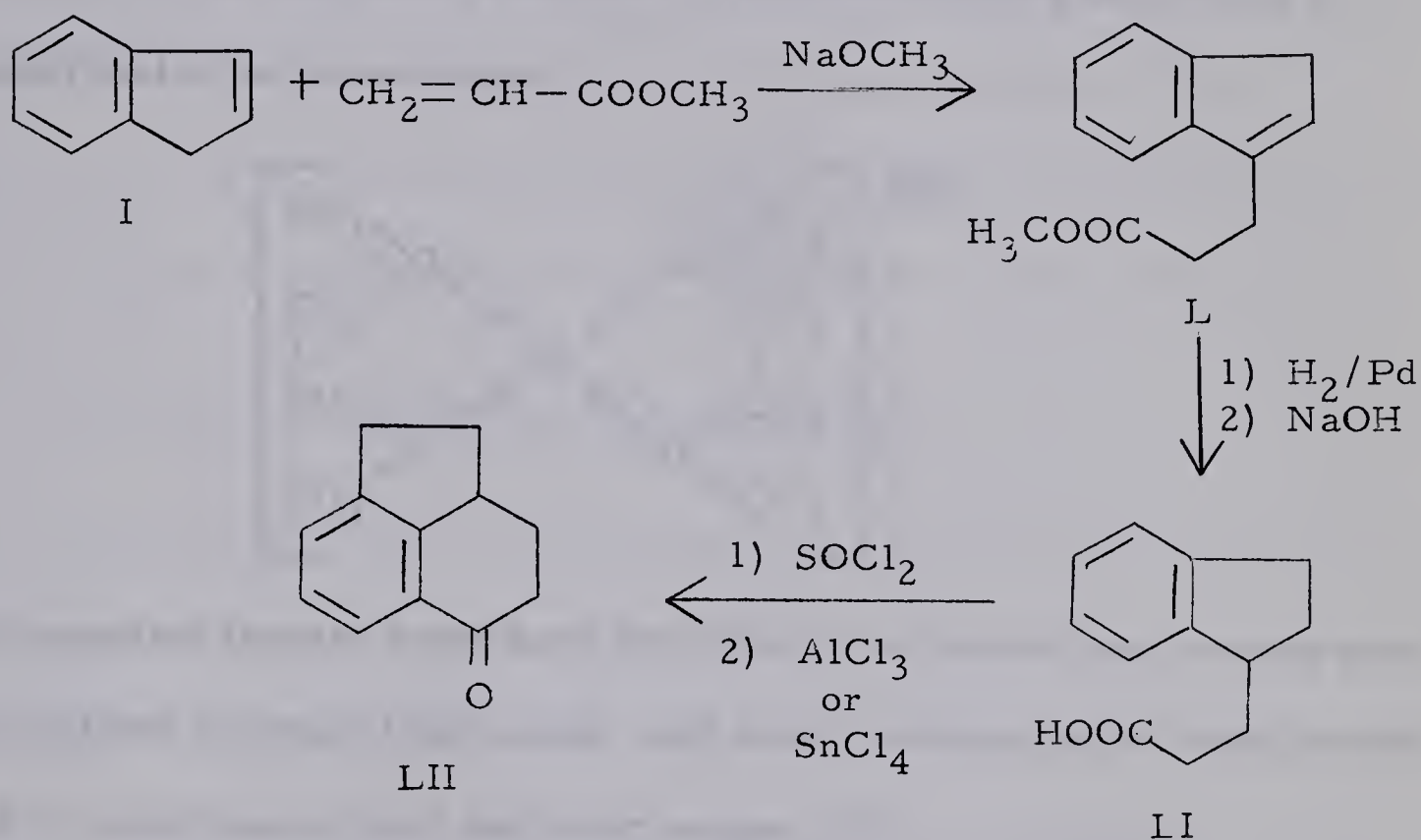
Similar reactions have been carried out using 1-tetralone derivatives, which require a Reformatsky reaction prior to cyclization. Reduction, as well as dehydrogenation, is of course required of the resulting keto derivative.

b. From Indene Derivatives.

1-Substituted indenenes are readily available intermediates for the synthesis of the acenaphthene nucleus. Cyclization by the



Friedel-Crafts method differs from the above reactions with respect to the position of the carbonyl group, which is now introduced in the cyclohexane ring. Needless to say, this change can be used to good advantage.



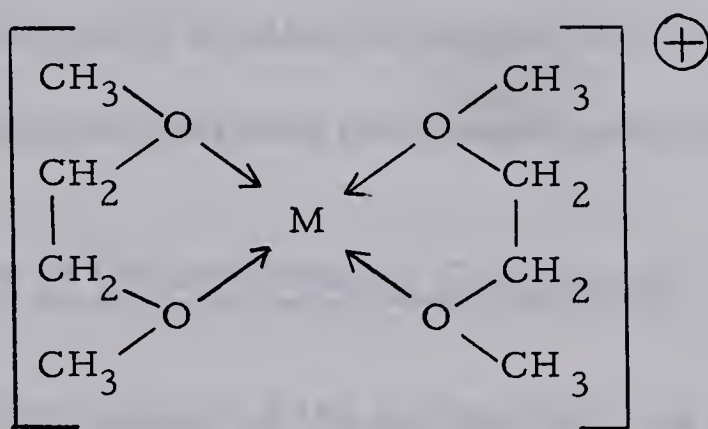
Reduction of ketone LII, followed by dehydration and dehydrogenation, would once again give the desired acenaphthene molecule.

### 3. The Solvent Role in Metalation.

In his review article, Schlosser (51) noted that the controlling factors in direct metalations are the acidity of the hydrocarbon, the electropositivity and particle size of the metal used, and the nature of the solvent. Similar factors were also used by Scherf and Brown (29, 30) to explain their observations. Their reported solvent order, 1,2-dimethoxyethane (DME)



$\rangle$  1,2-diethoxyethane (DEE)  $\simeq$  THF  $\rangle$  dioxan  $\rangle\rangle$  hexane agrees well with other known observations (70). Coates (71) emphasizes the point that organometallic reactions take place very much more readily in ethers with a high oxygen to carbon ratio. The efficacy of DME has been ascribed to its strong donor character, thereby reducing the energy of the alkali metal ion by solvation.



Other important factors necessary for effective solvation are the ring size in the chelated solvate of the cation, and steric interaction (or lack thereof) caused by substituents near the ether oxygen (72).

This latter observation has also been reported by Pudovik and Muratova (67). From their investigation on the effect of solvent structure on the reaction rate of lithium with naphthalene, acenaphthene, and phenanthrene, a sharp decrease in rate was found with increasing size of ether alkoxy groups. Consequently reaction in methyl ethyl ether was faster than in diethyl ether, while virtually no reaction took place in di-n-butyl ether. When acetal solvents were employed, methylal was superior to diethyl formal, while di-n-butyl formal was relatively unsatisfactory. The conclusion was reached that a change in the structure of the aromatic hydrocarbon had a



comparatively small effect on the reaction rate, being significantly smaller than the change in nature and structure of the solvents used in the reactions.

DME and cyclic ethers have also been used as solvents for the cleavage of aryl ethers by alkali metals (73). It was found that the reaction rate depended in some measure upon the solvent in the approximate order DME  $\rangle$  THF  $\rangle$  tetrahydropyran  $\gg$  methyltetrahydrofuran (MeTHF). The addition of small amounts of ether to hexane solutions of butyllithium and alkyl halides greatly accelerated the rate of metal-halogen exchange (74).

#### 4. The Nature of Organometallic Compounds..

Related to the nature of the solvent and, as mentioned earlier, to the application of  $pK_a$  scales, is the ionic state of organometallic compounds, discussed in recent publications (75, 76). In the first communication (75), the authors report direct evidence for the existence of two kinds of ion pairs from the electronic spectra of the fluorenyl carbanion ( $F^{\ominus}$ ). From the UV-visible spectra of the lithium, sodium, cesium, and tetrabutylammonium salts in various solvents such as toluene, dioxan, MeTHF, THF, DME, and pyridine, a sharp absorption peak at approximately  $355\text{ m}\mu$  was assigned to an intimate ion pair,  $F^{\ominus}M^{\oplus}$ . Maxima at  $373$  and  $521\text{ m}\mu$ , which appeared upon lowering the temperature, were believed to be due to solvent-separated ion pairs,  $F^{\ominus} \parallel M^{\oplus}$ . At  $25^{\circ}$ , in solvents possessing low dielectric constants (toluene 2.38D, dioxan 2.20D, MeTHF 4.6D), the ionic species were nearly completely made up of intimate ion pairs. In



THF (7.40D) and DME (7.10D) and pyridine(12.3D) , the lithium salts existed mainly as solvent-separated entities . In fact , at any temperature , the lithium salt always yielded the highest fraction of solvent-separated ion pairs , whereas the poorly solvated  $\text{Cs}^{\oplus}$  , or  $\text{NBu}_4^{\oplus}$  salts showed no evidence of solvent-separated ion pairs in THF , even at  $-80^{\circ}$  . Furthermore , the positions of the absorption bands were affected very little , if at all , by the polarity of the medium . Spectral studies of  $\text{F}^{\ominus}\text{Li}^{\oplus}$  in mixtures of dioxan and THF indicated that two molecules of THF were probably involved in the formation of  $\text{F}^{\ominus} \parallel \text{Li}^{\oplus}$  . The reactivity of solvent-separated ion pairs could approach that of the free carbanions , which could perhaps partly account for the higher reaction rates observed in more polar solvents .

Dixon and co-workers (76) have prepared complexes of 9-fluorenyllithium and such Lewis bases as THF , DME , and diethylether . From their investigations by means of NMR the following observations were made:

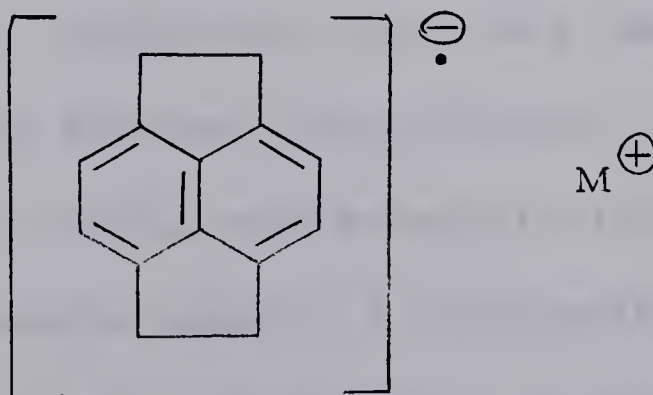
- a) THF and DME remain complexed with fluorenyllithium even when the salt was dried at room temperature for 48 hours , at less than 1 mm. pressure . Integrations of the spectra indicated a mole ratio of  $\text{THF}:\text{RLi} = 3.0-3.2$  , and of  $\text{DME}:\text{RLi} = 1.2-1.3$  .
- b) The resonance due to the remaining 9-proton in fluorenyllithium is shifted downfield by approximately 3 ppm from



its position in the fluorene spectrum.

- c) The protons of the complexed THF and DME are shifted upfield from their original positions.

From these data, it is postulated that: "The lithium cation is located directly above the plane of the aromatic carbanion, possibly in the  $\pi$  cloud. It is not intimately associated with the benzylic carbon in (or near) the ring plane, and is not located on the periphery of the ring system. In addition, the base molecules, which are strongly coordinated with the cation, are also located above the fluorenyl carbanion. As a consequence, both the cation and base are in the magnetic field due to the ring current." Supporting the idea of ion pairs is the example of "internal return", described by Cram (52), and the calculations of Ebel (77), which showed that carbon-alkali metal bonds are less polar than previously accepted. Additional studies (78) in the alkali radical-ion complex of pyracene (LIII) by means of electron spin resonance (ESR) indicated that the formation of ion pairs increases with increasing radius of the metal



LIII

ion, with decreasing dielectric constant and, consequently with increasing



temperature. The formation of ion pairs in the alkali metal-pyracene system depends on the counter ions, it increases in the order  $\text{Li} < \text{Na} < \text{K}$ . Mainly dissociated ions were present however, particularly in DME; some ion pairing occurred in THF.

## 5. Analytical Methods.

Due to the lack of available analytical tools, particularly GLC and NMR, results such as those reported by Campbell and co-workers (50) could not be positively construed, and as such were vague and indefinite. Although the metalation and alkylation of fluorene (29, 30) was followed by means of infrared spectroscopy, it was felt that the NMR technique would be a much more effective method. The NMR spectrum of indene, which is relatively simple, has been studied in detail (79, 80) while the spectrum of the indenyl anion has also been investigated (81). The former was found to be an  $\text{AKX}_2$  system, in which the two olefinic protons are separated by approximately 30 cps, and assignments could thus be made relatively easily. Furthermore, since the 1- and 3-positions of indene are so very much different from each other, it was anticipated that a clear distinction could be made between the two monomethyl isomers, and between the two dimethyl isomers, not only on the basis of the relative positions of the protons, but also by their coupling with neighboring hydrogen atoms. As it turned out, the NMR technique proved to be a very effective



tool indeed, a fact also shown by Bergson and Weidler (41).

It was felt that these principles could also be applied for the identification of the various substituted acenaphthenes. Although little work has been done in this field, a complete analysis of the acenaphthene spectrum, which showed some of the features of this system, has been reported (82).



## RESULTS AND DISCUSSION

This work is presented in two parts - Part I deals with indene, while Part II concerns itself with acenaphthene. All the pertinent NMR, IR, and UV spectra mentioned in these sections can be found at the end of the Discussion on p. 143 to 156.

### Part I - Indene.

#### Metalation of Indene and Alkylation of Metalated Indenes

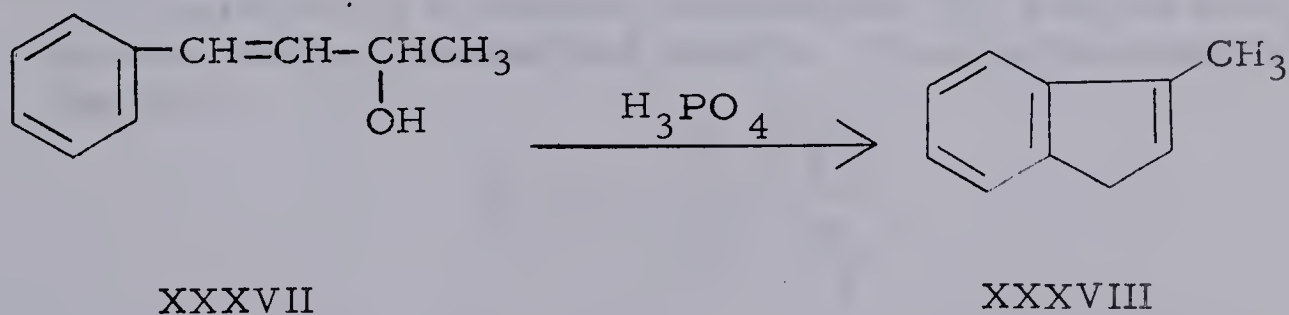
##### A. The Preparation of Methylindenes

By extending the work and results reported by Scherf and Brown (29, 30) on the metalation and alkylation of fluorene to the indene system, it was anticipated that methylation of the product from the reaction of equimolar quantities of indene and metal would afford a mixture of mono-methyl-, dimethyl-, and perhaps trimethylindene. Furthermore, due to the possibility of rearrangement of the double bond in the five-membered ring, isomers of the monomethyl- and dimethylindenes might be present. A few qualitative preliminary experiments seemed to support at least some of these ideas. It was thought advisable therefore to prepare the possible products of metalation and subsequent alkylation in order to have these compounds at hand for comparison with the alkylation products. These comparisons would be made by means of GLC retention times,



infrared spectra, and NMR spectra. Accordingly, the following compounds were prepared by authentic routes: 1-methylindene, 3-methylindene, 1,1-dimethylindene, 1,3-dimethylindene, and 1,1,3-trimethylindene, as well as 1-methylindan. At the start of this work, of these compounds only 1-methylindene and 1,1-dimethylindene had not been reported in the literature, although several reports on the preparation of 1-methylindene have appeared since that time (39-41).

In the course of devising a scheme to prepare 1-methylindene, it was thought advisable to repeat the work of Campbell and co-workers (50). In their study of the dehydration of some phenyl-substituted ethylenic carbinols, they reported the formation of a methylindene (XXXVIII) from the reaction between 3-hydroxy-1-phenyl-1-butene (XXXVII) and phosphoric acid. Although one might expect to obtain 1-methylindene (V) as a possible product from this reaction, these workers assigned the structure of 3-methylindene to the product.



Even though a rearrangement of the double bond is quite possible in acidic medium, it is also possible that such a rearrangement did not occur and that their assignment of structure was incorrect. The only evidence on



which their structure was based was the parachor\*, and the fact that only one reducible double bond was present in the molecule, indicative of an indene rather than 1-phenyl-1,3-butadiene or 1-phenyl-1,2-butadiene. The physical means to distinguish unequivocally between the two isomers, 1-methylindene and 3-methylindene were not available at that time, and chemical evidence for the support of structure XXXVIII was not presented. Although no mention was made by Campbell and co-workers whether it was the cis-or trans-3-hydroxy-1-phenyl-1-butene which was dehydrated, it may be assumed that both were investigated, since the syntheses of both compounds were described.

In this laboratory, trans-3-hydroxy-1-phenyl-1-butene (LIV) was readily prepared in 82% yield by treating freshly distilled cinnamaldehyde, which has the trans configuration (84), with excess methylmagnesium iodide (85). Attempted cyclizations of the alcohol by heating it with 85% phosphoric acid as had been done by Campbell (50), or with

---

\*The parachor is a constant relationship, for a given substance, between surface tension and density. This relationship is of the form

$$P = \frac{M \sqrt[4]{\gamma}}{\rho_l - \rho_g}$$

in which P is the parachor, M is the molecular weight,  $\gamma$  is the surface tension of the substance, in liquid form, at a given temperature, and  $\rho_l$  and  $\rho_g$  are the densities of the liquid and vapor at that temperature. The parachor has been used in deciding the structure of molecules and polymers. It must be used with caution, however, and a number of anomalies are known (83).

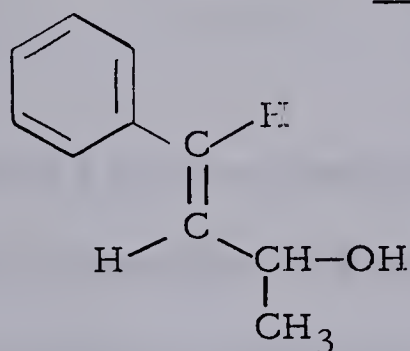


15-20% polyphosphoric acid on a steam bath for 30 to 60 minutes , failed.

The only product obtained was a high-boiling , viscous oil , which was not identified but may well have been polymeric phenylbutadiene (84).

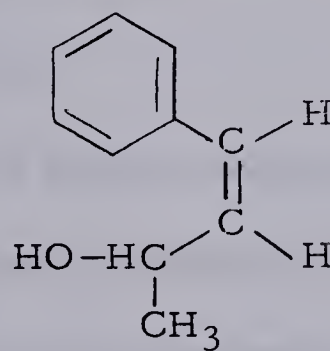
Replacement of the hydroxyl group by chlorine according to the method of Muskat and Herrman (84) , followed by treatment with anhydrous aluminum chloride in Skellysolve B also failed to give any of the desired indene. That these reactions failed to yield any of the cyclized product is in itself not surprising, since one is dealing with the trans configuration. But one report has indicated that the trans carbinol rearranges into the corresponding cis isomer with acid , in the presence of heat (84).

Accordingly, the possibility of cyclization starting with the trans isomer does exist, though this would depend upon the relative rates of isomerization to the cis compound and of polymerization. In view of the above results it seemed clear that the cis isomer would be preferred for cyclization.



trans

LIV



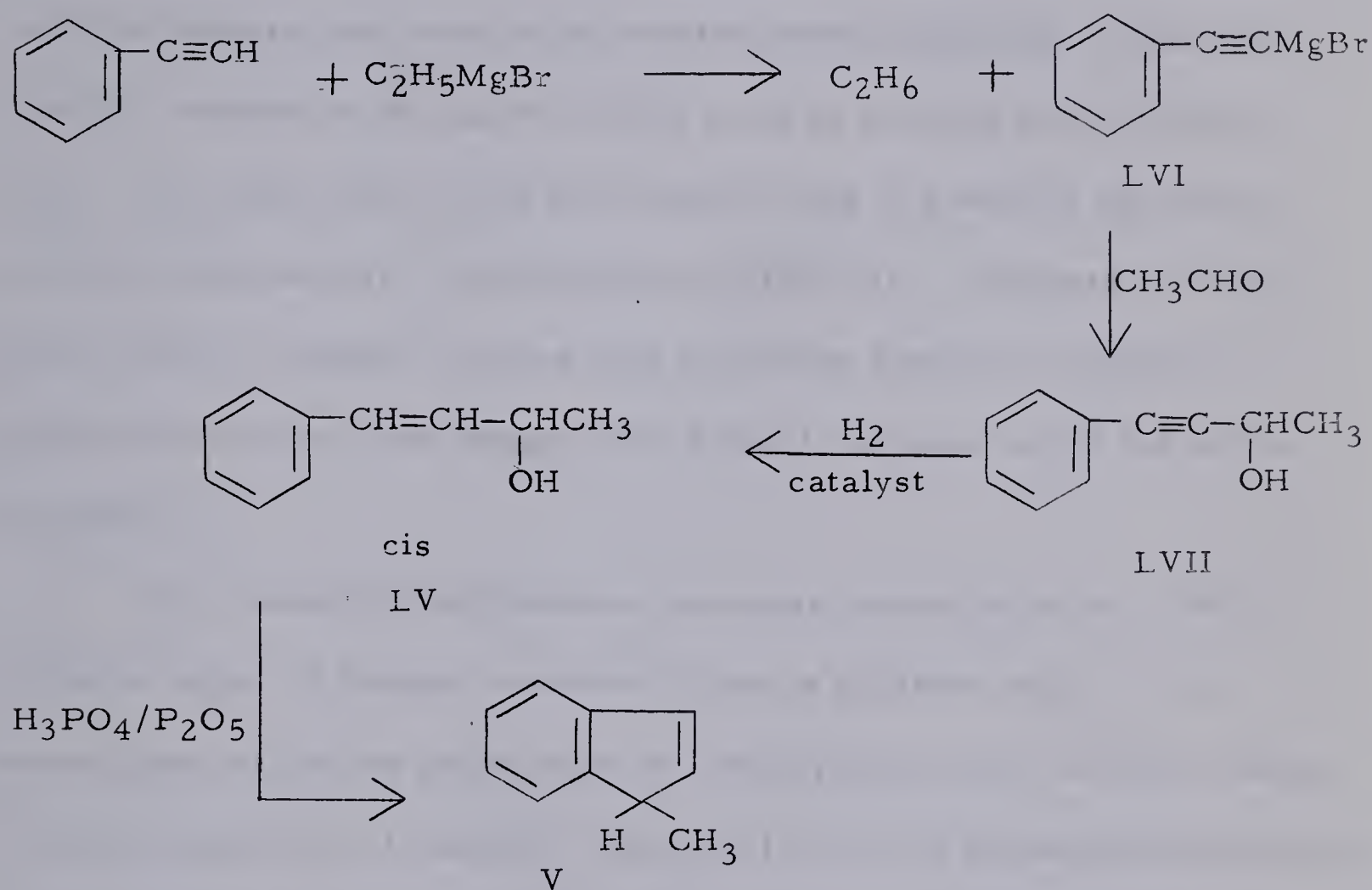
cis

LV

The cis-3-hydroxy-1-phenyl-1-butene (LV) was prepared by the method of Campbell et al. (50) with the modification that a catalyst other than the reported one was used during the reduction step. Thus , as



shown in the accompanying flowsheet, phenylethynylmagnesium bromide (LVI), prepared from ethylmagnesium bromide and phenylacetylene, when treated with an ethereal solution of acetaldehyde, gave pure 3-hydroxy-1-phenyl-1-butyne (LVII) in 65% yield.



Compound LVII was readily reduced with Raney nickel and the calculated amount of hydrogen, but the final product, obtained in 90% yield, was shown by GLC to consist of a mixture of four components, the largest being present to the extent of 60%. The use of Lindlar's catalyst ( $\text{Pd}/\text{CaCO}_3/\text{Pb}(\text{OAc})_2$ ) (86) however, gave a nearly colorless oil consisting of only two components in the approximate ratio 90:10. These were assumed to be the cis and trans carbinol respectively, since catalytic hydrogenation of triple bonds leads to mixtures of cis and trans olefins, in which the cis



isomer predominates (87, 88a). Heating and stirring the cis alcohol with polyphosphoric acid for 30 minutes, followed by steam distillation, afforded a low yield (10-15%) of a colorless oil which consisted of a mixture of products. By GLC retention times, approximately 20% of this isolated reaction mixture was found to be 3-methylindene (XXXVIII). The main fraction, present to the extent of 60%, could be isolated and purified by GLC. The NMR spectrum of this material was in complete agreement with that proposed for 1-methylindene (V) (Fig. 1). Attempts to cyclize cis-3-chloro-1-phenyl-1-butene with anhydrous aluminum chloride in petroleum ether at room temperature failed to produce any of the indene derivative.

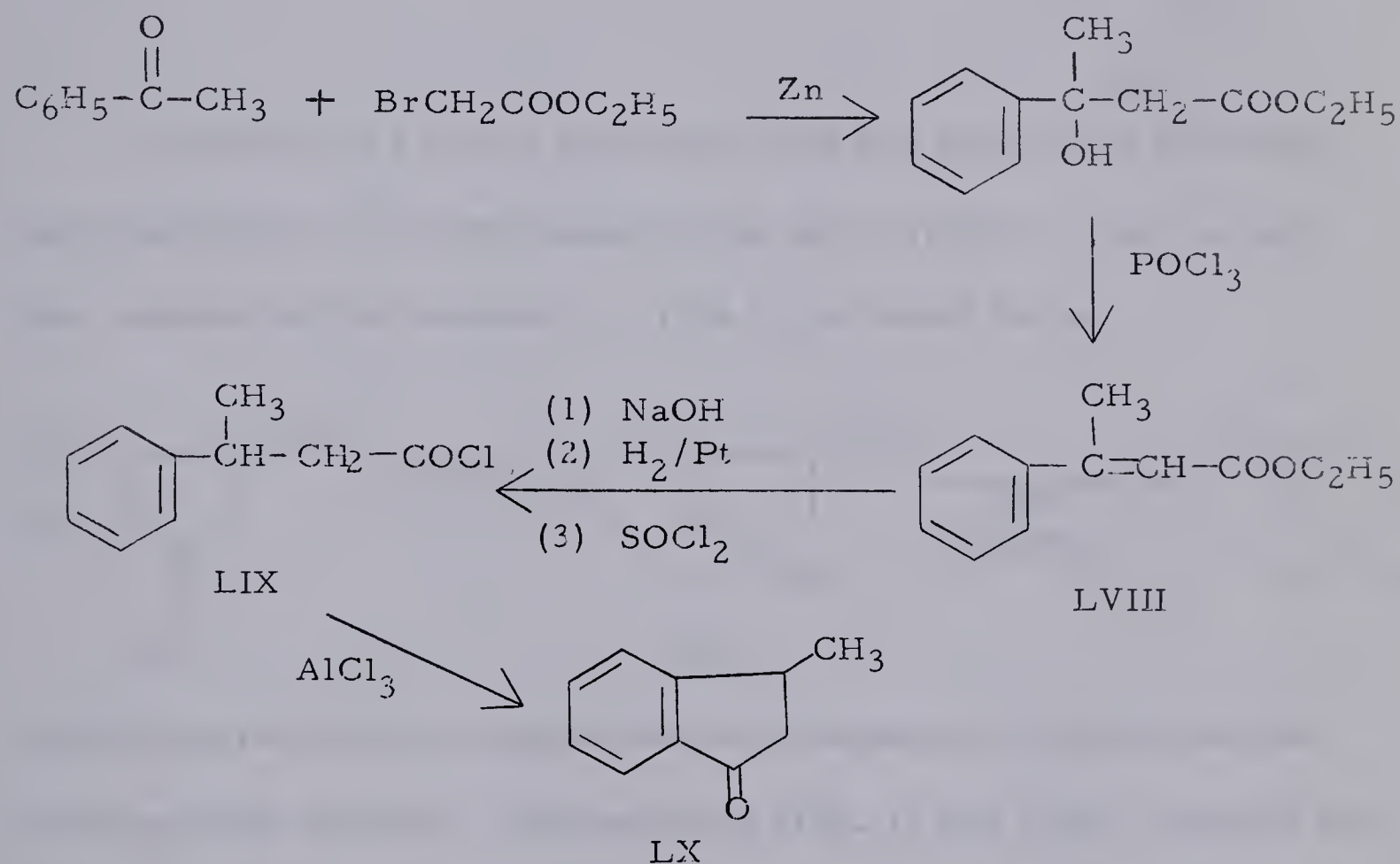
Since these cyclodehydration reactions turned out to be of little synthetic value, it became necessary to use a different route. The second approach to the preparation of 1-methylindene was one which began with the reduction of 3-methyl-1-indanone (LX), with subsequent dehydration of the resulting alcohol (LXI) in acidic medium to the indene. The success of this scheme depended upon the extent to which the expected product rearranged to the 3-substituted isomer under the reaction conditions. Very little was known concerning the acid-catalyzed rearrangement in these systems, but it was hoped that at least an equilibrium of the 1- and 3-methyl derivatives could be obtained, in view of our earlier results described above.

According to nearly all literature reports, the ketone (LX) has been



prepared by the Friedel-Crafts cyclization of  $\beta$ -phenylbutyryl chloride (LIX). This acid halide therefore was prepared from its precursor, ethyl  $\beta$ -methylcinnamate (LVIII), which in turn was synthesized by a Reformatsky reaction between acetophenone and ethyl bromoacetate, followed by dehydration of the product (50% overall yield of the ester) (89).

These reactions are shown graphically below.

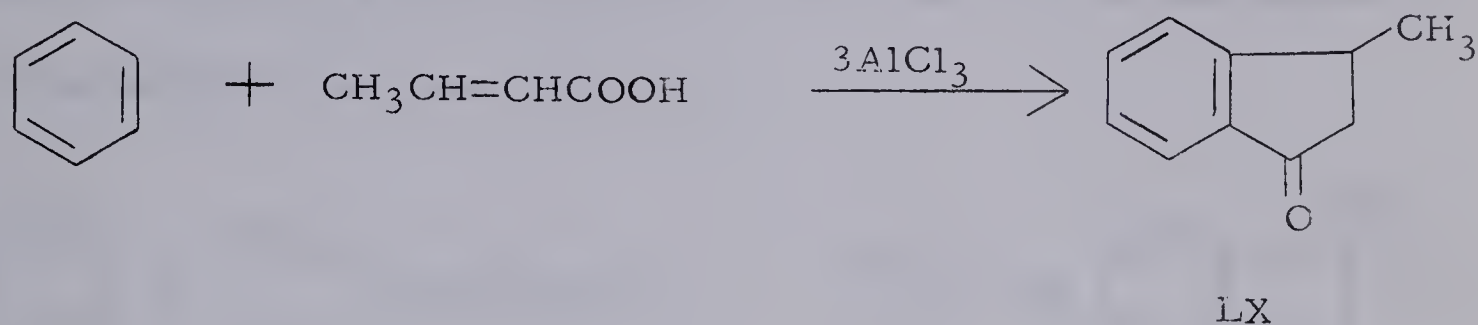


The subsequent reactions involving saponification of the ester, catalytic reduction of the resulting olefinic acid, then acid chloride formation, and final ring closure all took place readily, giving a final yield of the ketone of 56% based on the ester LVIII.

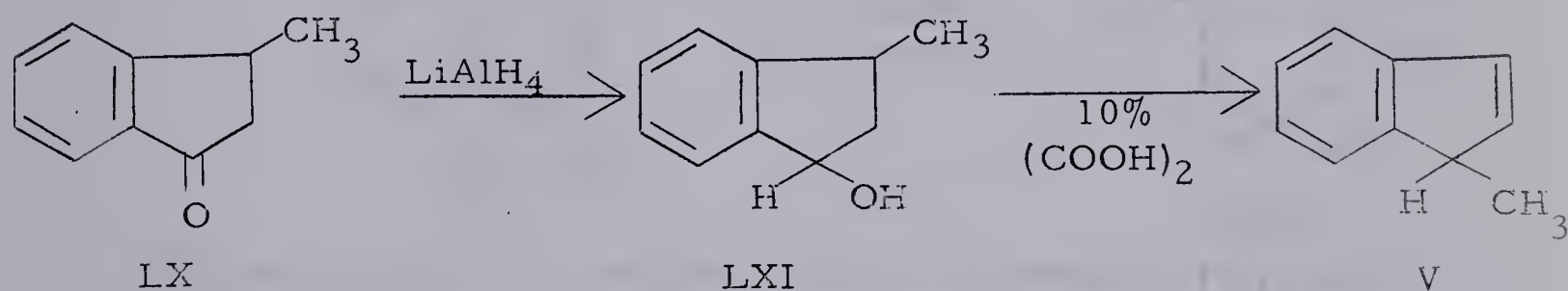
These rather elaborate syntheses were discarded in favor of a much simpler and quicker procedure, reported by Koelsch and co-workers (48). They refluxed a benzene solution of crotonic acid in the presence of three



equivalents of anhydrous aluminum chloride and obtained the indanone in one step. Unlimited quantities of the precursor could thus be obtained in excellent yield (82%).



At this time a recent publication (39) was discovered describing the preparation of 1-methylindene by the above synthetic route as had been planned in this laboratory. This is portrayed below.

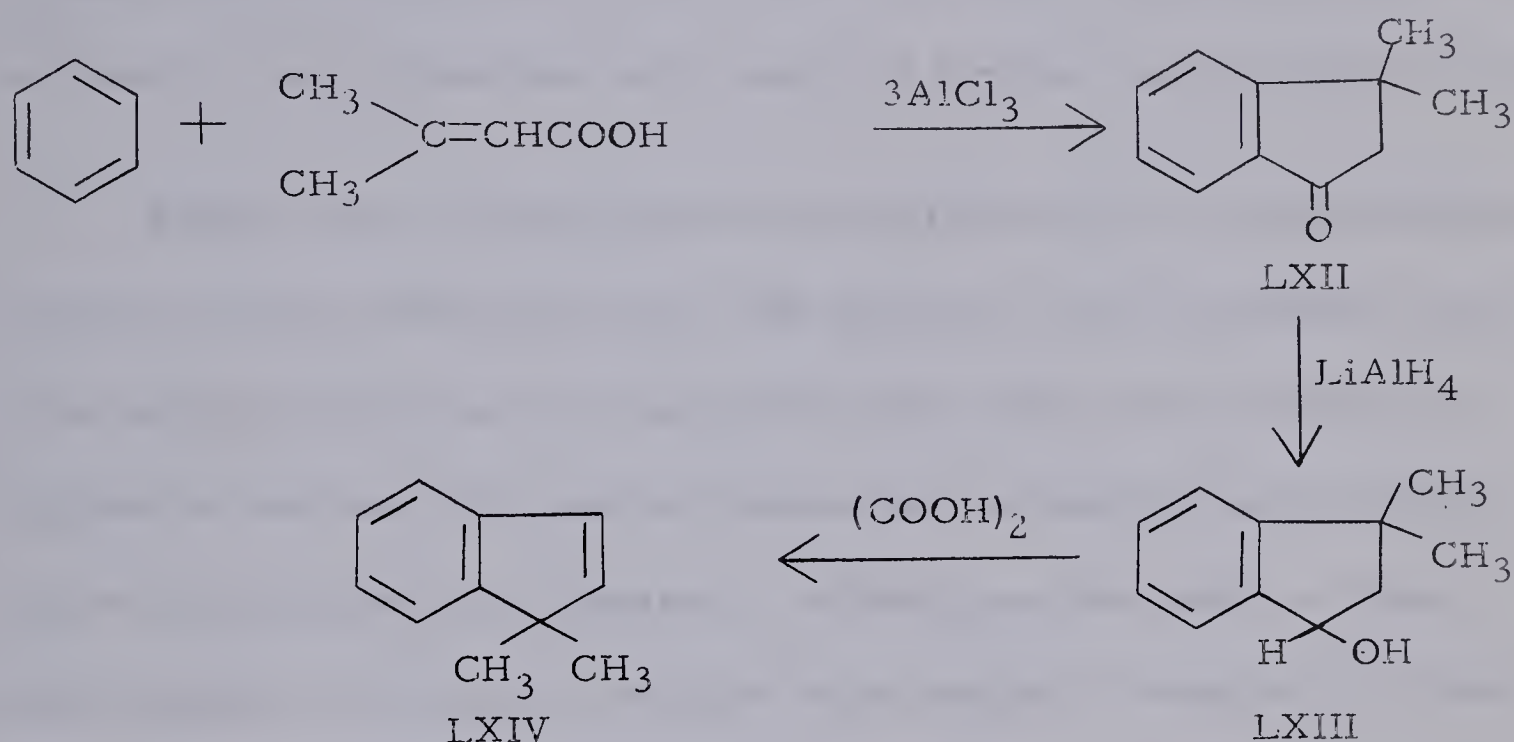


Their preparation was repeated here and compound V obtained and subjected to NMR analysis. The spectrum (Fig. 1) was quite consistent with the structure. Other workers also have supported this structure (40, 41) and have also shown that isomerization under acid conditions does not take place.

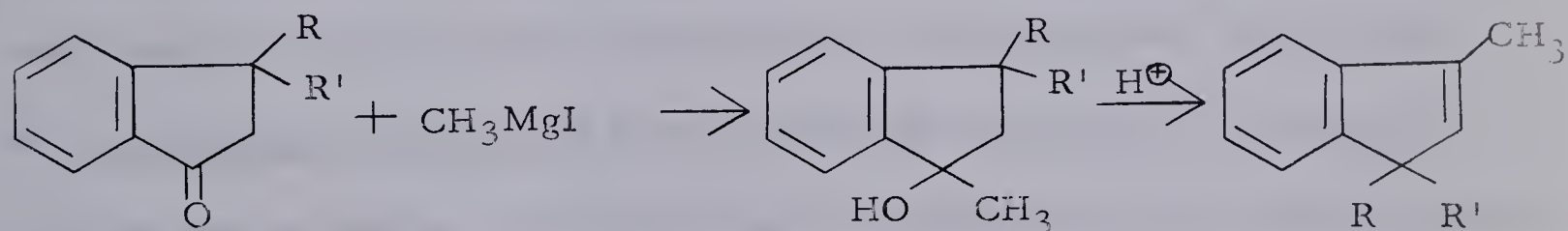
With the above available information at hand, it thus became possible, using the same general procedure of Yarboro *et al* (39), to synthesize the other unknown derivative, 1,1-dimethylindene (LXIV). By a Friedel-Crafts reaction, a mixture of benzene, 3-methylcrotonic acid and three mole-



equivalents of aluminum chloride gave 3,3-dimethyl-1-indanone (LXII) in 82% yield. Reduction of the ketone with lithium aluminum hydride (90) afforded 3,3-dimethyl-1-indanol (LXIII), which on dehydration with oxalic acid gave 1,1-dimethylindene in 50% yield. The NMR spectrum of this compound is shown in Fig. 3.



The preparations of 3-methyl- (91), 1,3-dimethyl- (92), and 1,1,3-trimethylindene (93) were all accomplished following known procedures, according to the general reaction:



For	3-methylindene (XXXVIII)	R = H	R' = H
	1,3-dimethylindene (LXV)	CH <sub>3</sub>	H
	1,1,3-trimethylindene (LXVI)	CH <sub>3</sub>	CH <sub>3</sub>

1-Methylindan (LXVII) was obtained by the reduction of 3-methylindene using



hydrogen and platinum oxide. The NMR spectra of the indenenes XXXVIII, LXV, and LXVI are shown in Figs. 4, 5, and 6 respectively, and are in complete agreement with the proposed structures.

B. Concerning the Mechanism of Metalation. Hydrogen evolution versus Birch reduction (94) in the reaction of lithium and potassium metal with indene, and comparison with results of similar reactions with fluorene.

Recent work (27) has shown that the formation of 9-fluorenyllithium from the reaction of lithium metal with fluorene in THF proceeds by way of the addition of the metal to the hydrocarbon, followed by reaction of this adduct with more fluorene to produce the metalated fluorene along with reduction products of fluorene. Although no conclusive evidence was available, the reduction products were thought to consist of a mixture of 1,2,3,4-tetrahydrofluorene and the cis and trans isomers of 1,2,3,4,10,11-hexahydrofluorene. Similarly, reduction products of biphenyl were observed when the 1:1 lithium metal-biphenyl adduct was used as a metalating agent for pseudoacidic hydrocarbons. Furthermore, it was found that no hydrogen was evolved from the lithium metal-fluorene reaction, although the formation of hydrogen has been indicated as one of the products of the reaction between fluorene and the alkali metals (29, 30). In another publication (28) it has been reported that the formation of triphenylmethylpotassium from the reaction of triphenylmethane with potassium metal in DME also produced no hydrogen. Solutions of the reaction mixture contained



various cleavage and reduction products , such as phenylcyclohexane , phenylcyclohexadienes , biphenyl and diphenylmethane (28).

Accordingly , since some of these results were contradictory and subject to argument , one aim of this work was to investigate the question of hydrogen production during the reaction of fluorene and indene with lithium or potassium metal.

Equal quantities (0.1 mole) of each of lithium (or potassium) metal and indene (or fluorene) were put into 100 ml of pure , dry DME in a standard 3-neck 250 ml flask , equipped with a magnetic stirrer , short condenser and gas collecting apparatus . All gases produced were collected by the downward displacement of water . The reaction mixture was refluxed until evolution of gas was complete and the metal either had all been consumed or no further reaction with the metal occurred (2-22 hours). The longer reaction times were carried out in some cases to ensure that no further gas evolution took place . Several blank runs were also made in which the metal was heated in refluxing solvent without fluorene or indene . The results of these experiments are shown in Table I , page 48 . Although this system is somewhat crude , it was quite adequate to show whether hydrogen gas was evolved in small , medium or large amounts . Care was taken to observe anhydrous conditions in all reactions (see experimental).

The blank runs , containing only metal and solvent , produced a volume of gas , due nearly completely to the expansion and displacement of



TABLE I

Production of hydrogen during the reaction of indene or fluorene with lithium or potassium metal in refluxing 1,2-dimethoxyethane (DME)\*

(0.1 mole of hydrocarbon + 0.1 gram-atom of metal in 100 ml of DME)

Expt. No.	Hydrocarbon	Metal Used	Amount of metal consumed, %	Time of reflux for complete gas evolution, hr	Volume of gas collected, ml	Amount of H <sub>2</sub> in collected gas %
1.	Nil	K	very little	} 2-5	200	1-2
2.	Nil	K	"		195	1-2
3.	Nil	Li	"		210	trace
4.	Nil	Li	"		210	trace
5.	indene	K	85	} 3-4	700	at least 50
6.	indene	K	88		725	(no analysis)
7.	indene	Li	80		900	at least 60
8.	indene	Li	77		800	(no analysis)
9.	fluorene	K	nearly all	} 3-4	350	35
10.	fluorene	K	"		390	(no analysis)
11.	fluorene	Li	80		220	2
12.	fluorene	Li	85-90		215	10
13.	fluorene	Li	(not estimated)	4 hours (incomplete reaction)	200	11

\*Generally the reflux was carried out until gas evolution ceased. In some cases reflux time was extended further even though more evolution of gas failed to take place.



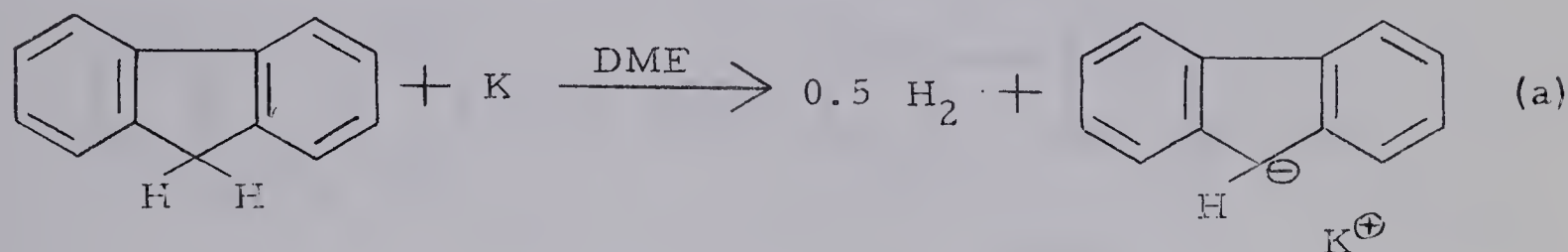
air , equal to 195-200 ml when potassium was used. This gas contained 1-2% of hydrogen as determined by mass spectrometry. When lithium was substituted for potassium , 210 ml of gas was obtained which contained only traces of hydrogen. Gas "evolution" was usually complete within 2 to 3 hours for potassium and 4 to 5 hours for lithium, and no further increase in volume of collected material was found in the several runs made where blanks were refluxed for nearly half a day.

A mixture of indene and potassium gave 700-725 ml of gas , over 50% of which was hydrogen (presumably 500 ml), while indene and lithium evolved 800-900 ml, over 60% of which was hydrogen (presumably 600-700 ml). Gas evolution ceased in both cases after 3-4 hours and no further increase was noted in cases where the reaction was continued for an additional 12 hours.

When a mixture of fluorene and potassium in DME was refluxed , 350-390 ml of gas was collected (an increase of 150-190 ml above the blank value) , at least 35% of which was hydrogen. However , the reaction between lithium and fluorene gave a total volume of gas , 200-220 ml , which mass spectrometry showed to contain about 10% of hydrogen , although in one case out of the three cited only 2% of the collected gas was hydrogen. Small peaks at  $m/e=15$  and 27 did begin to appear however , when long periods of reflux were used. These presumably were due to methane and ethylene respectively , which could arise from solvent-metal interaction (see p. 83).



It is quite apparent that fluorene reacts with potassium to give substantial amounts of hydrogen—but not in the amount equal to that expected if the only reaction between fluorene and the metal were one of hydrogen evolution according to equation (a).



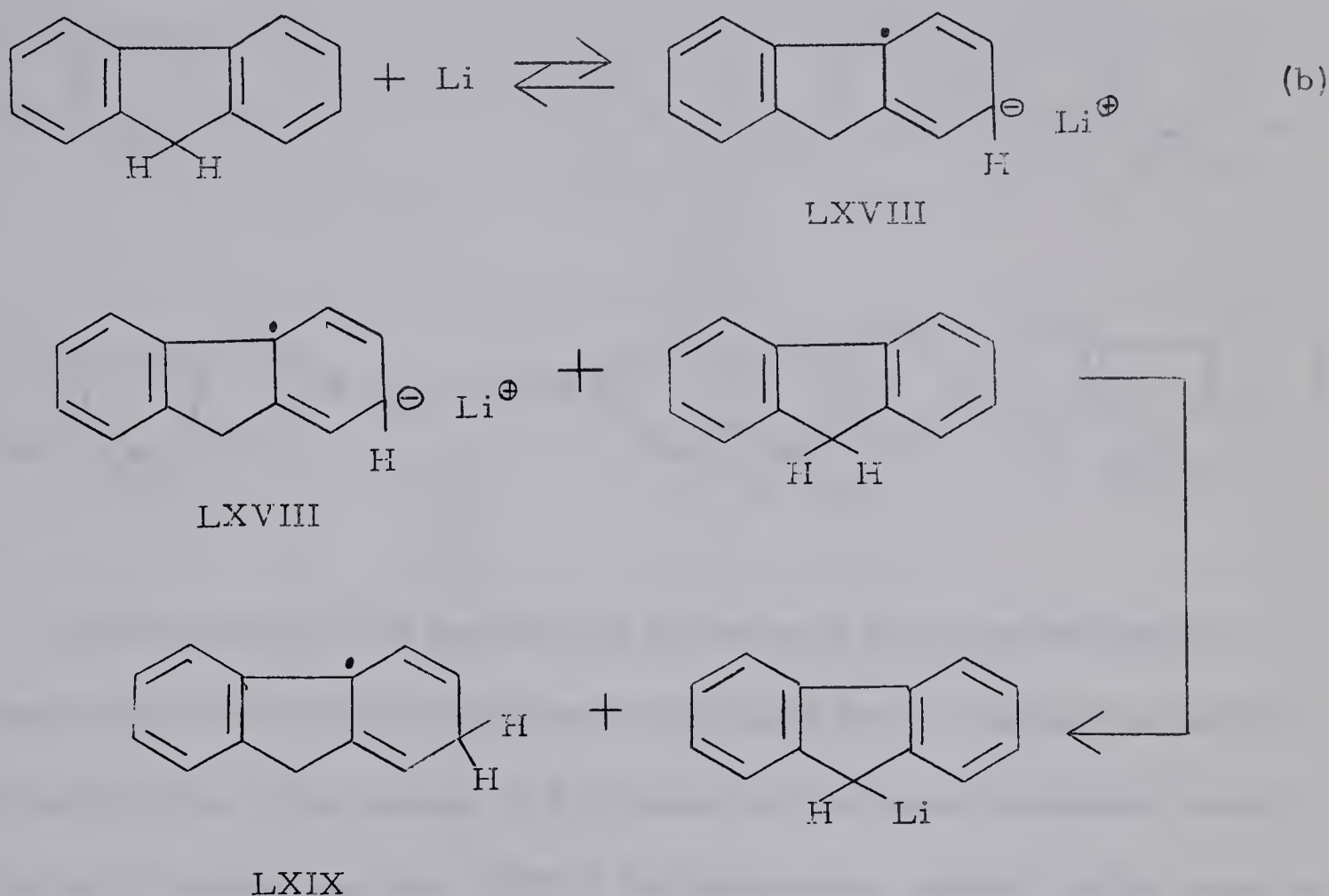
This type of reaction can be compared to the well-known, similar reaction of cyclopentadiene with the alkali metals (71). Roughly 11-14% of that theoretically required by equation (a) was actually produced. On the other hand, the reaction of lithium with fluorene definitely gave hydrogen, but only in small amounts — about 1.5% of that theoretically required by equation (a). The detection of hydrogen evolution in the present case, but none in the work reported by Eisch and Kaska (27) can be accounted for by the different conditions employed. The latter authors used a larger volume of solvent (400 ml of tetrahydrofuran containing 0.1 mole of fluorene) and room temperature conditions, while the present work employed 100 ml of solvent (DME) containing the same amount of fluorene, and reflux temperature. The latter conditions would promote elimination of small amounts of dissolved hydrogen.

From the results in Table I it is quite evident that, in addition to reaction (a), a second reaction, consuming the bulk of the metal, has occurred — nearly completely (98-99%) in the case of lithium and fluorene,



but to a somewhat lesser extent (85%) with potassium and fluorene.

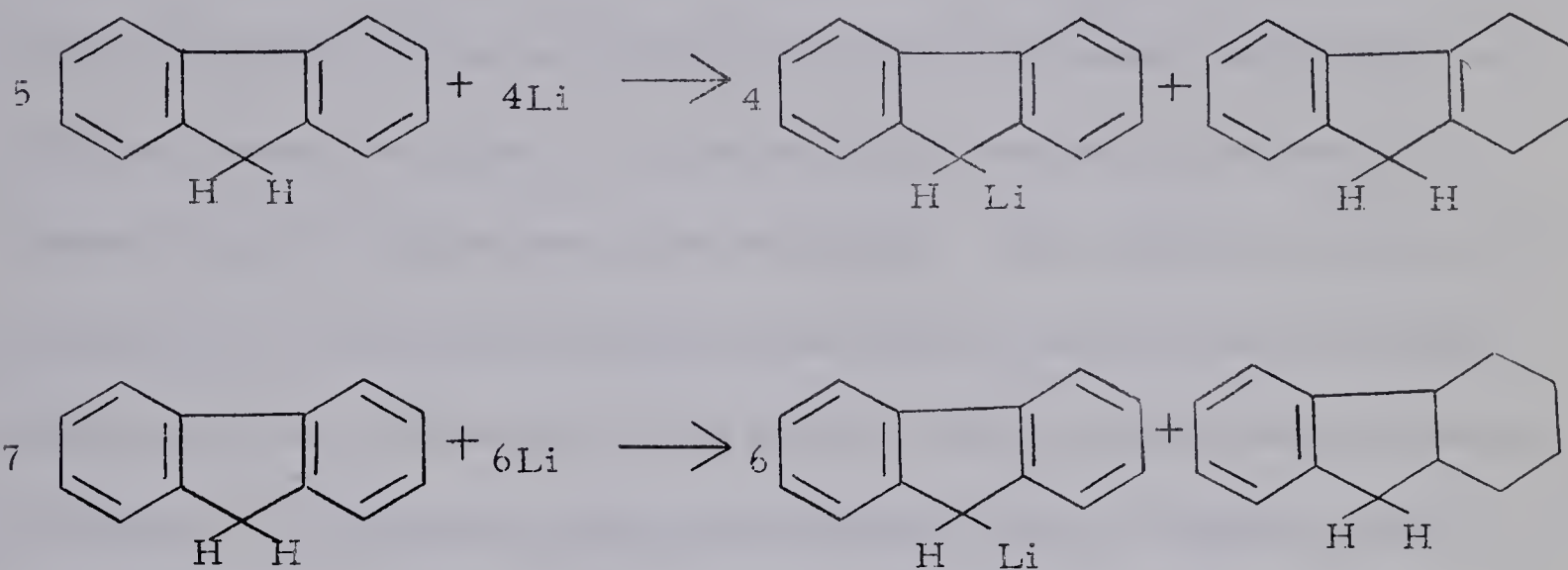
Undoubtedly this occurs by way of reaction (b) as pointed out by Eisch and Kaska (27), leading to a Birch-type of reduction (94) of a portion of the fluorene to tetrahydro- and hexahydrofluorenes.



The resulting radical LXIX could gain another electron from unreacted lithium to form an anion which could metalate more fluorene. As Eisch and Kaska (27) pointed out, certain lithium adducts of partially reduced aromatic systems are kinetically very good metalating agents, and partially reduced fluorenes should form kinetically stronger radical anion bases. Through successive reactions a portion of the fluorene thereby becomes reduced to tetrahydro- and hexahydrofluorenes. The observation (27) that 1.0 mole of fluorene reacted with 0.82 gram-atom of lithium to



provide 0.83 mole of 9-fluorenyllithium, lent further support to the formation of tetrahydro- and hexahydrofluorenes. This can easily be seen from the following two overall reactions, where 0.80 and 0.86 gram-atom of lithium per mole of fluorene are required respectively.



In comparison, the reaction of indene with either potassium or lithium metal in DME gave much more hydrogen gas. Taking the blanks into consideration, the amount of hydrogen evolved when potassium metal reacted with indene was about 40% of the theoretical amount, while reaction with lithium gave about 50% of that required by an equation similar to (a). Obviously in these two cases as well, the metal was consumed not only by the route expressed by equation (a), but also by one such as shown in equation (b). This is supported by the isolation of indan as one of the products of the reaction, to the extent of 15-17% of the product when potassium was used, but only 8-10% when lithium metal was employed (Table II, page 56). Further mention of the two competing reaction mechanisms will be made in a later section (p. 55, 57).



It was noted that in the case of lithium metal, the source as well as particle size is apparently important. Larger pieces of BDH lithium metal (98%), after 24 hours of heating in refluxing DME, were consumed to the extent of 48-50%, and gave 23% of the product as indan. Tiny pieces of Fisher Scientific lithium were 93% consumed in 20 hours, but yielded only 9% of the product as indan. In this particular section of the work only Fisher Scientific lithium was used throughout. The difference in reactivity between the two batches of lithium metal could in part be due to a slight difference in the composition of the metals, although information regarding the content of impurities could not be obtained from the supply houses. Sodium, which is often a chief contaminant, has been shown to have a pronounced catalytic effect on the ease of preparation of certain organo-lithium compounds (95, cf. 96). This may have been the cause of the differences observed.

It is well-known that cyclopentadiene reacts with an alkali metal to yield a half mole of hydrogen, plus the cyclopentadienyl anion (71). Cyclopentadiene therefore, reacts with a metal completely according to the equation:



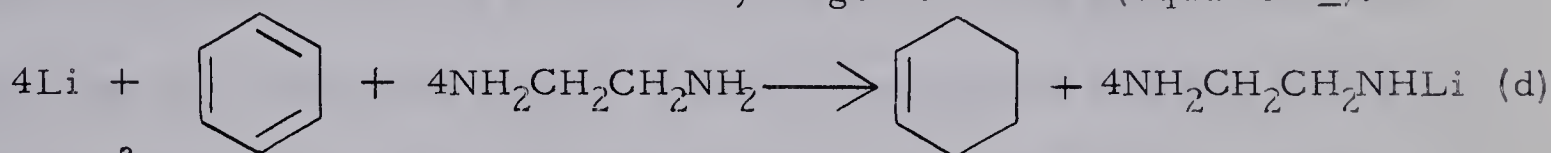
Indene (a benzocyclopentadiene) does this to the extent of 40-50%, while fluorene (a dibenzocyclopentadiene) reacts at the most 15% in this fashion. This order seems to correspond to the relative acidities of these three hydrocarbons (5).



In connection with the observed competitive reaction mechanisms in which hydrogen evolution appears to be more prevalent at higher temperatures the work of Beumel and Harris (97) supports our views. These workers have shown that in the reaction of lithium metal with ethylenediamine in benzene, a competition occurs between direct reaction of the metal with the diamine to produce hydrogen gas plus the lithium amide (equation c),



and addition of the metal to the benzene followed by a Birch-type of reduction and lithium amide formation without hydrogen evolution (equation d).



Above 85° reaction (c) becomes very fast, with the evolution of a considerable amount of hydrogen. At lower temperatures, hydrogen evolution according to process (c) is insignificant, and reaction (d) predominates, giving nearly quantitative reduction.

### C. Methylation of Indenyllithium and Indenylpotassium.

In preparation for the alkylation, the metalated indenenes were made by heating equivalent amounts (0.1 mole) of indene and metal in 100 ml of refluxing DME under nitrogen for a specified time. The unreacted metal was then removed as much as possible from the cooled solution and excess methyl iodide ( $\geq 0.15$  mole) added dropwise, keeping the temperature of the solution at 0-5°. The reaction mixture was subsequently analyzed by gas-liquid chromatography (GLC). Results of the methylations are



assembled in Table II.

The following observations are made from the data in Table II.

1. The amount of metal consumed appears to be nearly the same regardless of the duration of the reflux period during the metalation, within the limits shown. Whenever equivalent amounts of lithium and indene were employed, 80-90% of the metal reacted, whether the mixture was refluxed for 5 or 22 hours, while with potassium 85-90% of the metal was consumed within the limits of 2 to 16.5 hours. However, in the case of potassium, when a 2:1 molar ratio of metal to indene was used, more than one equivalent amount of metal disappeared and this only when the reflux period was extended to 20 hours. In no case where excess lithium was employed was more than one equivalent of metal consumed, even though the reflux time was extended to 72 hours (cf. Table VII, page 86).
2. The amount of indan formed is nearly reproducibly the same regardless of the time of reflux of metal with indene or whether a two-fold excess of metal was used. The reaction with lithium gave 8-10% of indan while that of potassium yielded 15-17% of the product as indan.

These two observations (1 and 2), coupled with the fact that the reaction of both lithium and potassium with indene produced substantial amounts of hydrogen (Table I), strongly support the concept of a competition between two different reactions of the metal with indene. One involves the reaction of indene as an "acid", producing hydrogen (equation e) and the other involves the formation of the metal adduct which then metalates more



TABLE II

Preparation and methylation of 1-indenyllithium and 1-indenylpotassium in 1,2-dimethoxyethane\*

Metal Used	Metal to indene ratio	Time of metal- ation, (hr.)	Amount of metal consumed, %	Reaction products, mole % of total product							Unknown Products %	Total Recovery %
				Indan	Indene	1-Methyl- indene	3-Methyl- indene	1,1-Di- methyl- indene	1,3-Di- methyl- indene	1,1,3- Tri- methyl- indene		
Li**	1	5	~90	9	7	20	51	2	11	0	0	
Li	1	5	~85	8	9	53	19	1	10	0	0	
Li	1	5	~80	8	9	43	27	2	10	0	1	
Li	1	22	~80	10	10	41	26	2	10	0	1	
Li***	1	18.5	~87	9	10	51	23	~0.5	6	0	trace	83
				8	8	42	19	~0.5	5	0	trace	
K**	1	2	~85	17	12	0	53	2	14	0	2	
K	1	16.5	~90	15	8	0	59	3	13	trace	2	
K	1	15	~90	15	8	0	60	2	12	1	2	
K	2	3	~45	16	7	0	59	3	12	2	1	
K	2	20	55-60	16	2	0	54	5	14	8	1	
K***	1	3	~83	15	8	0	64	2	10	0	1	93
				15	8	0	58	2	9	0	1	

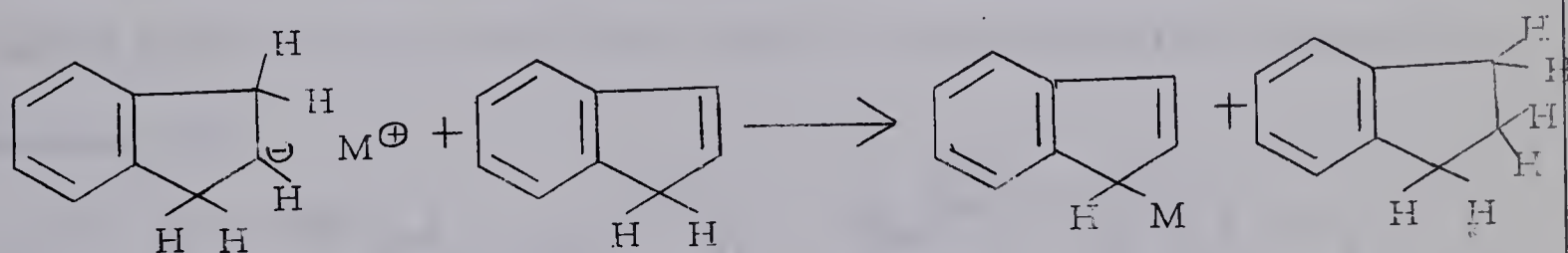
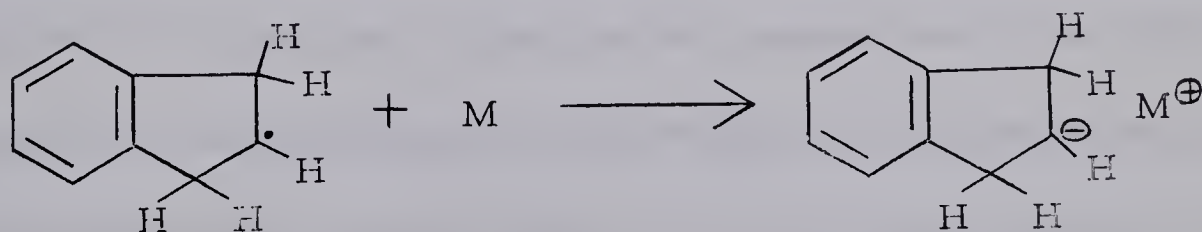
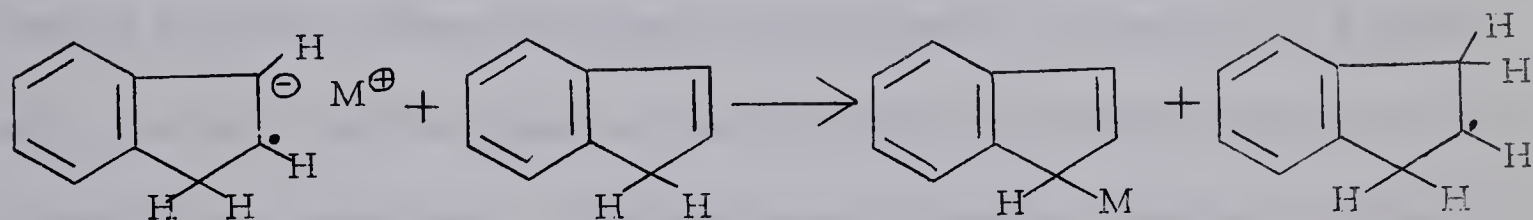
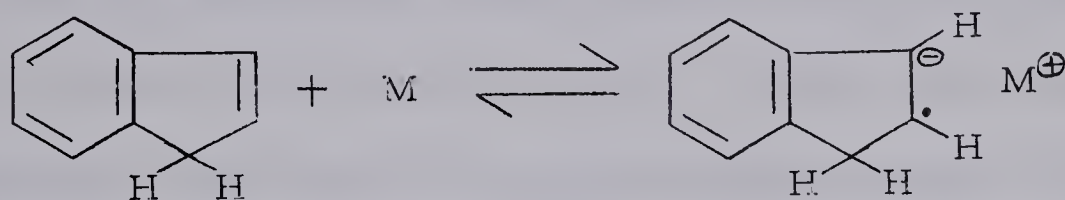
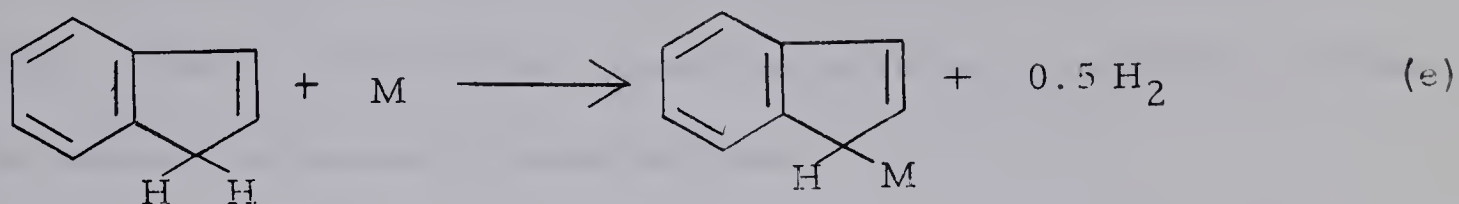
\* 0.1 mole of indene was dissolved in 100 ml of dimethoxyethane and refluxed with the appropriate amount of metal. Methylations were performed at 0-5°.

\*\* Methylations were done at room temperature in these two cases.

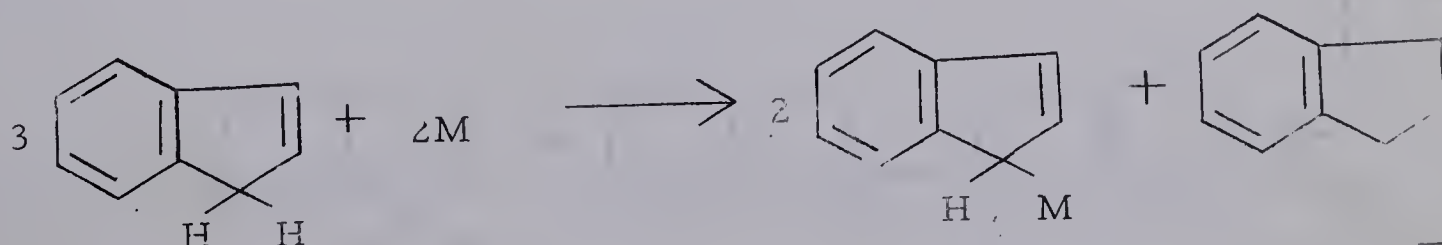
\*\*\* In these two cases a material balance was made to estimate total recovery, using tert-butylbenzene as an internal standard. The upper line of figures represents the percentages of each substance based on the total amount of isolated product. The lower line is the percentage of each substance based upon the indene



indene with simultaneous formation of reduced indene (equation f) via a Birch-type of reduction (94).



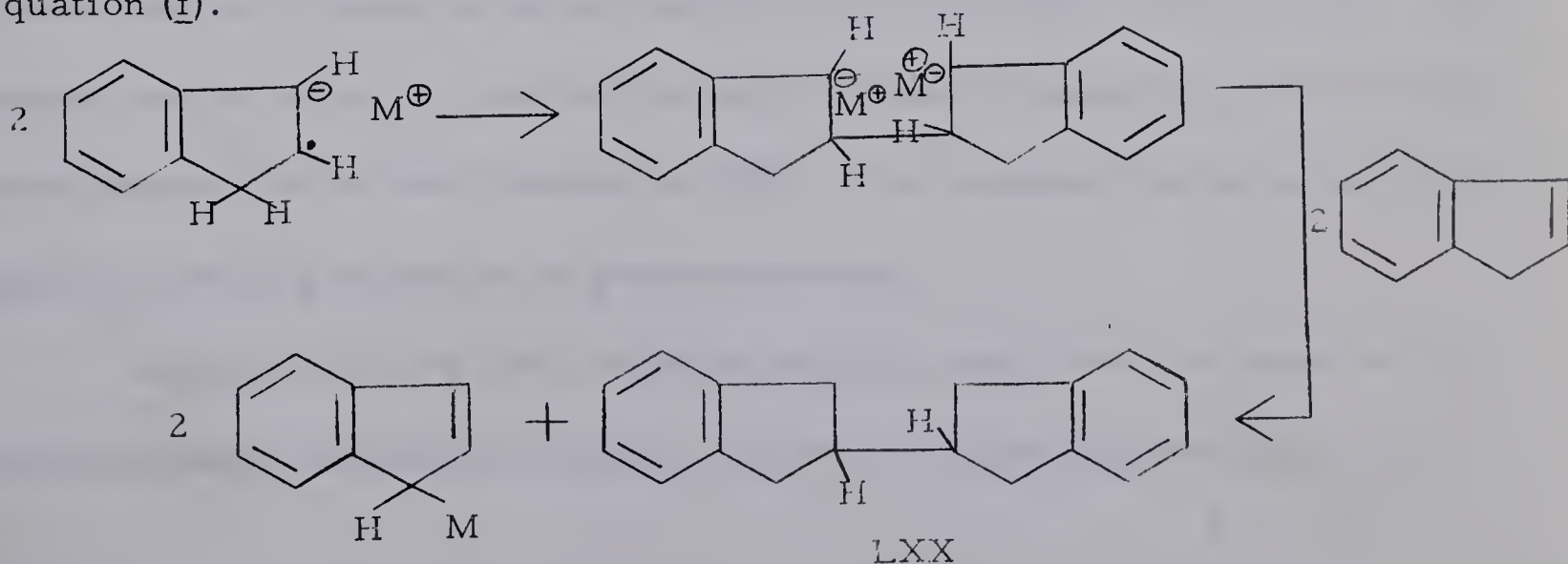
The overall reaction:





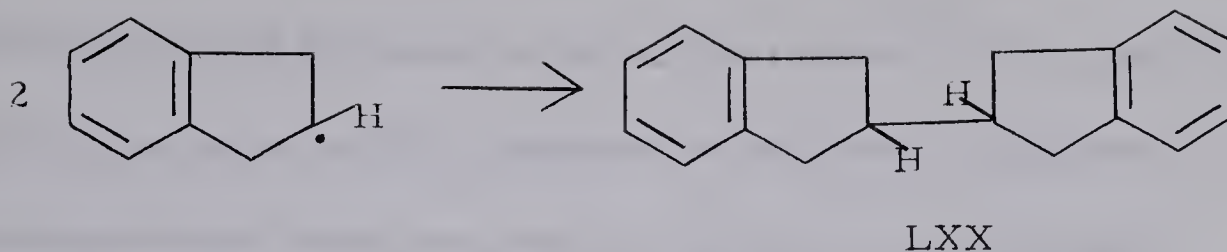
The exact nature of each reaction step in equation (f) is unknown, of course, although there seems to be little doubt about the reversible nature of the first step. Recent work (98) has shown the existence of equilibria between metallic sodium and aromatic hydrocarbons.

Equation (e) predicts that equimolar amounts of indene and metal react to produce 0.5 mole of hydrogen. Equation (f) predicts that one mole of indene will react with  $2/3$  of a gram-atomic weight of metal yielding  $1/3$  of a mole of indan and  $2/3$  of a mole of the metalated indene. Since the amount of metal consumed actually lies between  $2/3$  and 1.0 of a gram-atomic weight, and hydrogen as well as indan is produced, both reactions (e) and (f) are required. Furthermore, from the reaction of lithium with indene there has been isolated a small amount (few hundred milligrams) of the compound 2,2'-biindanyl, identified by comparison of its NMR, IR, mass spectrum, and melting point (and mixed melting point) with those of an authentic specimen prepared from  $\alpha, \alpha'$ -dibromo-o-xylene and diethyl malonate (99). The formation of 2,2'-biindanyl is feasible from either the radical anion, or the indanyl free radical, two intermediates suggested in equation (f).





or



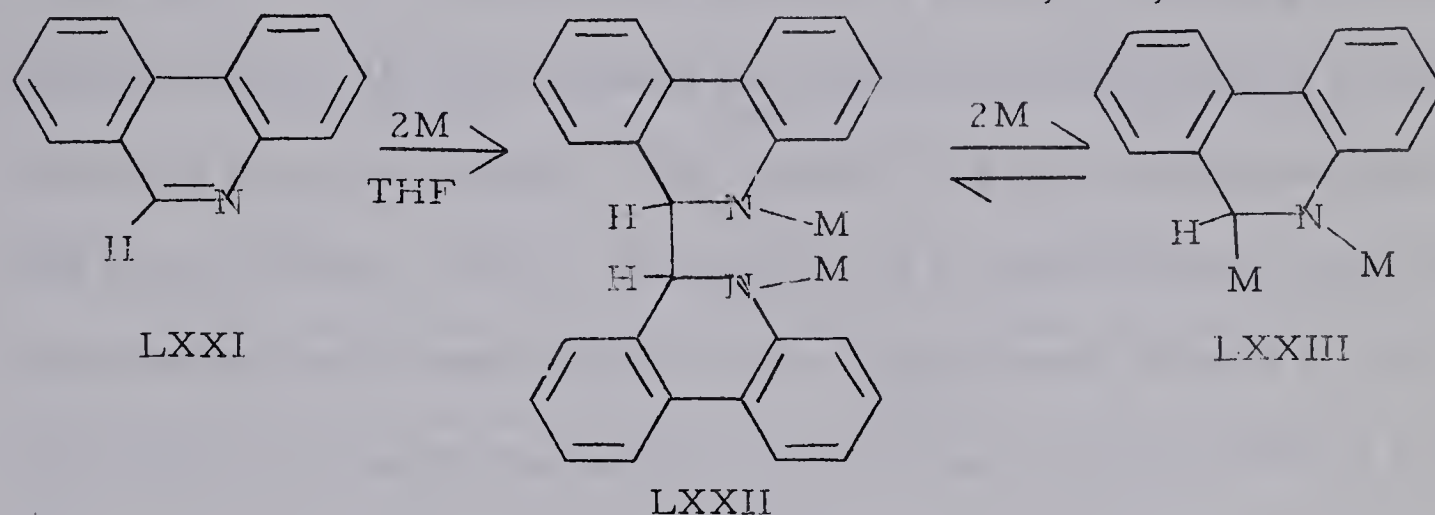
The first dimerization reaction is similar in nature to that of the known styrene radical anion, with the resulting dianion being able to metalate more unreacted indene. The negative charges being in a benzylic position, one might expect some stabilization due to resonance, and as such the dianion might be able to survive long enough to be methylated by added methyl iodide. No methylated biindanyl was detected, but this is not surprising in view of the small amount of the parent compound, 2,2'-biindanyl, that was found. Both coupling reactions should therefore be feasible.

Attempts to isolate this biindanyl from the reaction involving potassium were fruitless. The failure to obtain biindanyl in this instance might be due to the greater electropositive nature of the potassium metal, resulting in reduction of the indanyl free radical before it could dimerize. There was in all cases some unreacted metal left which could do this. The larger amount of indan found in the metalation with potassium (15-17%) than from the metalation with lithium (8-10%) can be rationalized in terms of the greater reducing capability of potassium metal.

Simple reduction and reductive coupling reactions are known to occur quite frequently during metalations, not only with hydrocarbons, but also



with heterocycles. An example of the latter case is the behavior of phenanthridine(LXXI) towards the active metals Li, Na, and Mg-MgI<sub>2</sub> (100). With lithium metal in THF solution for example, a dihydro as well as a biphenanthridyl derivative were isolated after hydrolysis.



3. The amount of recovered starting material, indene, is nearly constant, regardless of the length of time for metalation, when equivalent amounts of indene and metal are used. No significant change in the amount of recoverable indene occurred when a 2:1 ratio of metal to indene was heated in refluxing DME for a relatively short time (up to 3 hours with potassium metal and 20 hours with lithium metal-Table VII\*). But extended time of reflux resulted in lowered recovery of starting material (2% rather than 8% recovery of indene when a 2:1 ratio of potassium to indene was heated for 20 hours in refluxing DME; 6% rather than 9% of indene recovered when a 2:1 ratio of lithium to indene was heated in refluxing DME for 72 hours-Table VII\*). The decreased indene did not show up as a corresponding increase in the amount of indan, but might have appeared, via further methylation by some route as an increase in the quantity of dimethyl- or trimethylindene. A larger amount of the polyalkylated indene did in fact



occur under these conditions.

4. The total amount of monomethylindene (both 1-methylindene and 3-methylindene) is nearly constant regardless of the length of time of metalation. This is to be expected from a reaction involving two competing pathways (e) and (f), which would then lead to the formation of a definite amount of metalated indene. For lithium, the total varied between 67% and 74% of the product. At 0°, methylation of 1-indenyllithium gave both 1-methylindene and 3-methylindene in the approximate ratio of 2:1, but methylation at room temperature reversed this since the ratio of 1-methylindene to 3-methylindene was now 2:5.

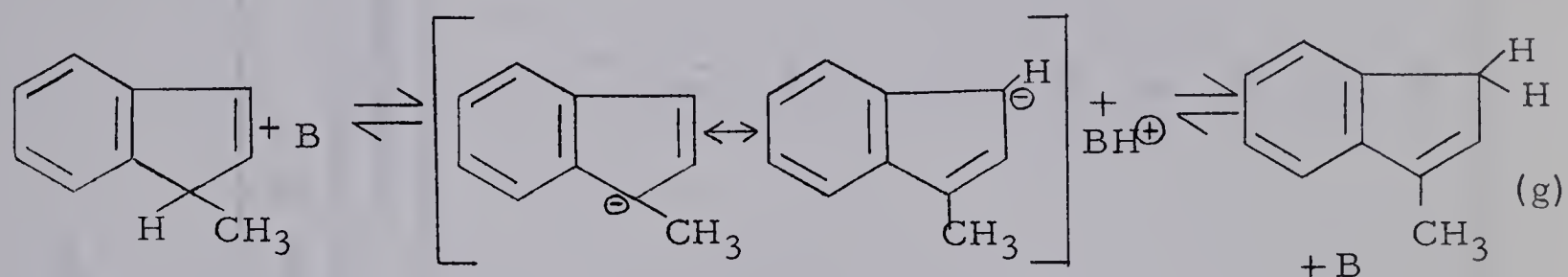
For potassium metal, the total amount of monomethylindene was 59-64% of the product except when the ratio of potassium metal to indene during metalation was 2:1, and then only for reflux periods considerably greater than 15 hours. In this case, 54% of the product was monomethylindene (Table II). The accompanying increase in di- and trimethylated indene could readily account for this. It is also to be noted that a 2-hour metalation period yielded less (53%) of the monomethylindene, but also more recoverable indene. This result is quite likely due to incomplete metalation in this time. A further significant point is that all of the monomethylindene obtained is the 3-isomer, whether the methylation was carried out at 0° or at room temperature.

#### The Isomerization of 1-Methylindene

The isolation of both 1-methylindene and 3-methylindene from the



methylation of 1-indenyllithium, but only 3-methylindene from the methylation of 1-indenylpotassium is no doubt due to the isomerization of the initially-formed 1-methylindene in the presence of basic reagents, possibly through an equation such as (g).



In the presence of the strong base, 1-indenylpotassium, this conversion was rapid ( $\sim 10$  sec) and the equilibrium indicated in equation (g) appeared to be completely on the side of 3-methylindene. Increase in temperature accelerated this conversion as shown by the greater proportion of 3-methylindene obtained in the methylation of 1-indenyllithium at room temperature than at  $0^\circ$ .

(i) Thermal Isomerization of 1-methylindene.

The isomerization can be accomplished by heat alone. When 1-methylindene was refluxed in DME ( $83^\circ/700$  mm) for 24 hours, no change to 3-methylindene was perceived. But when 1-methylindene itself was heated to reflux ( $\sim 184^\circ/700$  mm) and aliquots, withdrawn periodically, were analyzed by GLC, the material was converted 94% to 3-methylindene in 80 minutes as shown in Table III.

The data do not fit any simple kinetic order, no doubt due to the polymerization which accompanied isomerization at this temperature, as well as change of reflux temperature as the isomerization progressed. After 80 minutes much of the material had polymerized as shown by the viscous material clinging to the walls of the flask. Indenes are known



TABLE III

Isomerization of refluxing 1-methylindene to 3-methylindene

(Initial reflux temperature,  $\sim 184^{\circ}/700$  mm)

Reflux time, min.	Product analysis, %	
	1-methylindene	3-methylindene
0	99	1
10	93	7
20	79	21
30	62	38
40	47	53
50	27	73
60	22	78
70	13	87
80	6	94
120	4	96
180	4	96



to polymerize readily when exposed to light and heat (45a, 101).

The thermal isomerization appears to involve an equilibrium, since no change in the 4:96 ratio of 1-methylindene to 3-methylindene occurred during the period of reflux between 120 and 180 minutes. The same proportion of these two isomers was obtained when 3-methylindene was refluxed for 7 hours (Table IV). The exact position of the equilibrium is not certain since it is not known what the relative rates of polymerization are for 1-methylindene and 3-methylindene. The isomerization, however, occurs much more rapidly than does the polymerization.

Shortly after our isomerization results had appeared in print (102), similar work by Cristol, Plenat, and Huebner (101) confirmed our views. These workers also found that isomerization by heat alone could be achieved, although the presence of a metallic catalyst (10% Pd on charcoal) increased the rate of isomerization considerably. In the absence of catalyst, stirring 1-methylindene at room temperature for 150 days did not effect any change at all, but heating at 164° for 2 hours yielded 19.9% of the 3-methyl isomer, while 96% of the latter was formed after a two-hour period at 222°. The high-temperature rearrangement (222°) was also accompanied by the formation of 1.4% of 1-methylindan, even though no catalyst was present. Similarly, by heating 3-methylindene at 222° for 1 hour, 94.4% of the starting material remained, while 4.2% of 1-methylindene and 1.4% of 1-methylindan had formed. When they repeated the experiment in the presence of 10 and 50 mg. of catalyst, results indicated a 3.7:96.3 and

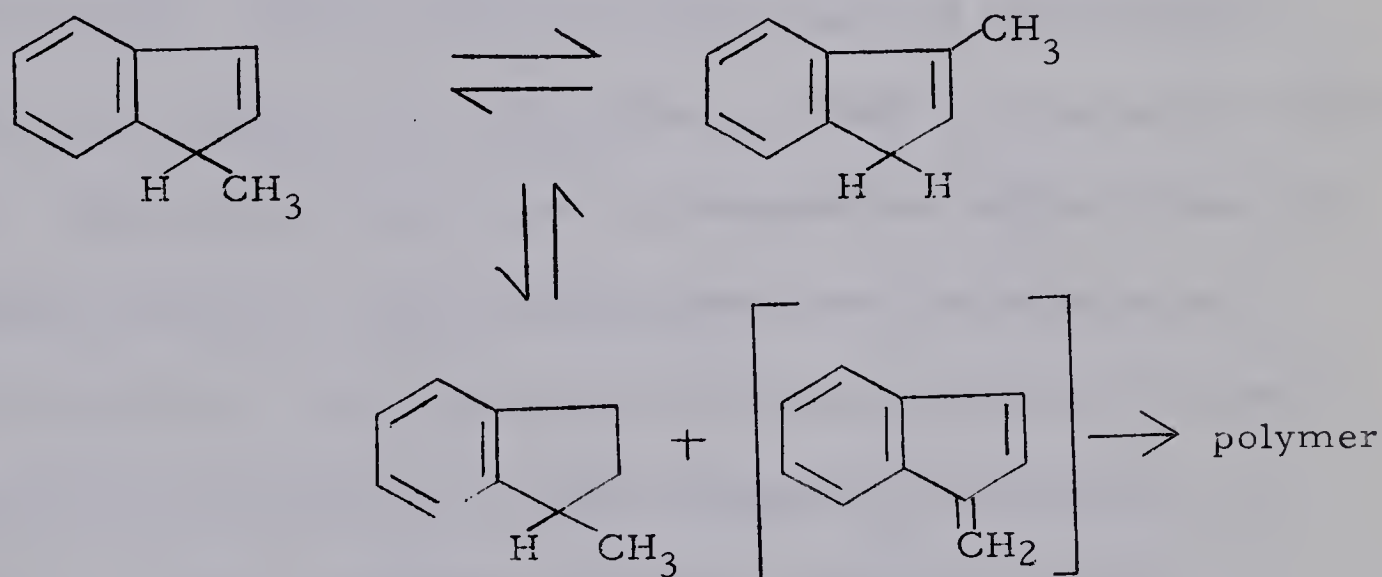


TABLE IV  
Isomerization of refluxing 3-methylindene to 1-methylindene  
(Initial reflux temperature,  $\sim 200^{\circ}/700$  mm)

Expt.	Reflux time, hours	Product analysis, %	
		1-methylindene	3-methylindene
1	0.5	2	98
	1.0	3	97
	2.0	4	96
	3.0	4	96
	4.0	4.5	95.5
2	3.0	3	97
	5.0	4	96
	6.0	4	96
	7.0	4	96



3.4-96.6 ratio of 1-methylindene to 3-methylindene respectively, after correction had been made for the presence of reduction product (23.5% and 61.5% respectively). Obviously, their work is in complete agreement with that of ours, with the exception that we did not observe any 1-methylindan. The formation of the reduction product, even in the absence of palladium catalyst, was believed by the French authors to be due to a hydrogenation-dehydrogenation reaction at these high temperatures, leading to the formation of 1-methylindan and 1-methyleneindene. The latter hydrocarbon is known to polymerize quite readily (19), and could account for the observed polymeric residue.



The equilibrium between 1- and 3-methylindene is therefore believed to be "perturbed" by the disproportionation reaction (101).

Additional thermal rearrangements of 5- and 6-methoxyindenes have very recently been reported with similar observations by Winter et al. (42).

(ii) Base-catalyzed isomerization of 1-methylindene



As expected, the base-catalyzed isomerization of 1-methylindene proceeded much more rapidly than did the thermal isomerization, and the rate of this transformation depended upon the strength of the base. The results of several qualitative tests are shown in Table V, and indicate that the effectiveness of the bases used were, in order of decreasing catalytic power, 1-indenylpotassium > methanolic NaOH > 1-indenyl-lithium > pyridine.

The base-catalyzed isomerization of 1-methylindene eventually yielded only 3-methylindene. This is supported by the fact that only 3-methylindene was obtained from the reaction of 1-indenylpotassium with methyl iodide. Further support for this view was obtained from the treatment of a solution of 3-methylindene in DME with methanolic sodium hydroxide. Addition of the base gave an instantaneous yellow colour, due to the indenyl carbanion, which became darker when the mixture was shaken for 2 minutes. No conversion of the 3-methylindene to 1-methylindene was detectable by GLC. Further shaking of the mixture for an additional 15 or 30 minutes failed to alter the result (cf. expt. No. 5, Table V).

The difference between the base-catalyzed and the thermal isomerization may be due to the fact that in the former case we are dealing with the two contributing structures below, existing perhaps as free ions or ion pairs, wherein the right hand form is practically completely predominant.

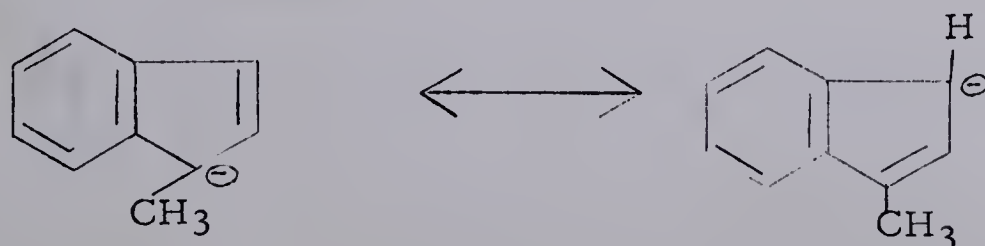




TABLE V

Isomerization of 1-methylindene in the presence of base

(Each run was made with 0.3 ml of 1-methylindene in 1 ml of DME and the base added)

Expt. No.	Base	Time of reaction and conditions	Color, observations	Conversion to 3-methylindene, %
1.	Solid K* (about 2 mm cubed)	Shaken 5 sec. at room temperature	slight yellow	1-2
2.	"	Shaken 10 sec. at room temperature	dark red	95
3.	Solid Li* (about 2 mm cubed)	Shaken 5 min. at room temperature	slight yellow	1-2
4.	"	Boiled 3-4 min., volume of solution reduced by 1/4	orange	9
5.	2 drops** methanolic NaOH	Shaken at room temperature for - 5 sec. - 15 sec. - 120 sec.	immediate orange which darkened on standing at room temperature	20 32 89
6.	4 drops pyridine	Heated 15 min. under reflux	yellow	8

\* Very little of the Li or K was consumed.

\*\* Made from 3 pellets of NaOH in 10 ml of methyl alcohol.



This argument, however, may be questionable. Even if the postulated free ions or ion pairs are present to an appreciable extent, they would involve an equilibrium with the respective neutral molecules, and thus would depend upon the free molecule equilibrium.

The difference between the room temperature base-catalyzed rearrangement and the thermal rearrangement can be adequately explained on the basis of simple chemical thermodynamics. From the thermal rearrangement a 96:4 equilibrium was reached between 3-methylindene and 1-methylindene at approximately 200°C. From the equation

$$-\Delta F = 2.303 R T \log_{10} K$$

where  $K$  = the equilibrium constant between the two isomers

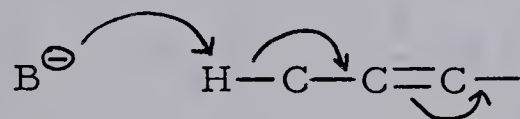
$$\begin{aligned} &= \frac{[3\text{-methylindene}]}{[1\text{-methylindene}]} \\ &= \frac{96}{4} \\ &= 24 \end{aligned}$$

the free energy difference between the two isomers we found to be approximately 3 kcal/mole. By using this value, the equilibrium constant at room temperature could be calculated, and was found to be  $\sim 150$ . Hence at room temperature one would expect to find virtually none of the 1-methylindene and more than 99% of the 3-methylindene.

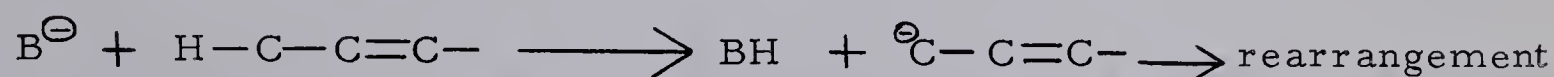
In relation to the thermodynamic stabilities of the neutral molecules, one would expect the 3-methylindene to be the more stable isomer, since it contains the more highly alkylated olefinic bond (88b, 103).



Evidence against free indenyl anions such as mentioned above, and against equation (g), has been brought forth by Bergson and Weidler (41). From their kinetic studies on the proton mobility in the indene ring system they favor, not a base-catalyzed concerted mechanism, e.g.

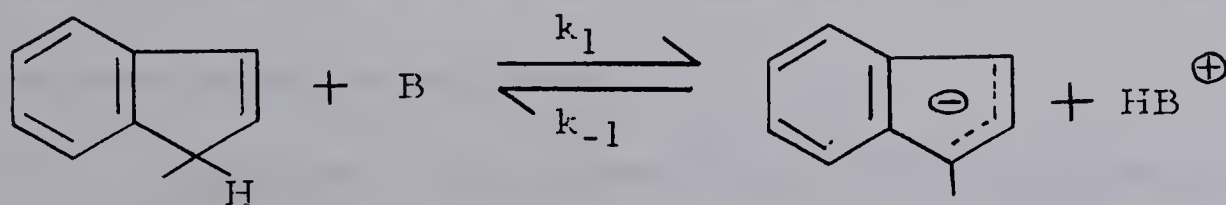


nor a stepwise mechanism involving free anions, e.g.



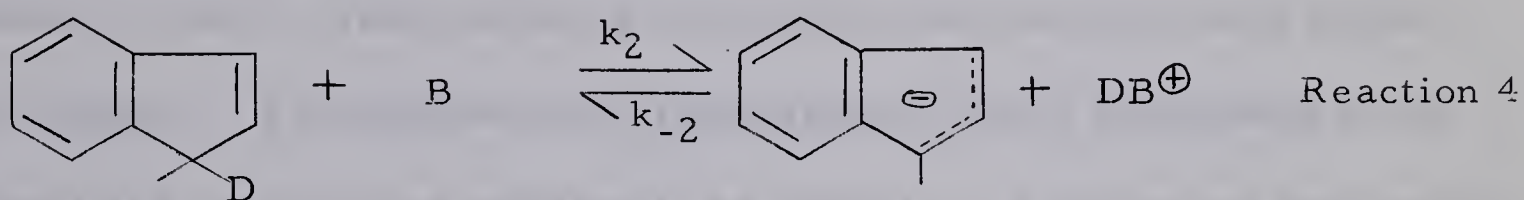
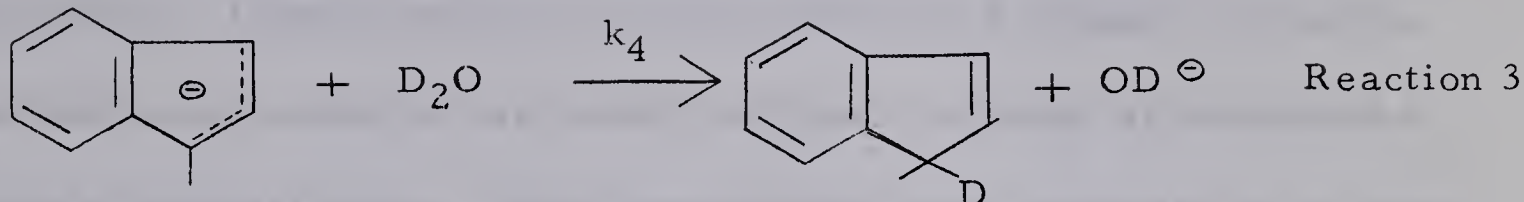
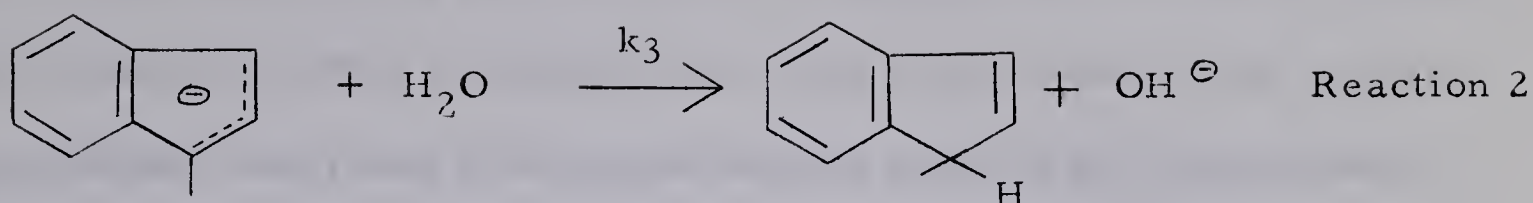
but rather a pure intramolecular hydrogen migration catalyzed by base.

Studying the hydrogen exchange between indene and deuterium oxide at room temperature in pyridine solution with triethylamine as a catalyst by the NMR technique, they observed that the exchange rate obeyed pseudo-first-order kinetics, and that it was proportional to the base concentration and the initial concentration of the deuterium oxide. Substitution by deuterium occurred at the 1- and 3-positions. They considered the following four reactions:



Reaction 1





and found that  $k_3 [h]$  and  $k_4 [d] \ll k_{-1} \sim k_{-2}$ , where  $h$  and  $d$  are the concentration of  $\text{H}_2\text{O}$ -protons and  $\text{D}_2\text{O}$ -deutrons respectively. This means that the recombination rate of the indenyl "anion"- $\text{BH}^+$  pair is much higher than is the rate of reaction of the indenyl "anion" with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . Kinetically, however, they found it impossible to distinguish between any one mechanism from the above scheme, and reactions 1-4 contain formally all possible mechanisms from stepwise to concerted, with a continuous transition between these two extremes.

Additional observations from the NMR analysis led Bergson and Weidler to believe that a pure concerted or stepwise mechanism could not



be the only one operating in the system. In addition, the rate of racemization of optically active 1-methylindene, also proportional to the catalyst concentration, was found to be approximately equal to the isomerization rate, and very much greater than the rate of hydrogen-deuterium exchange with solvent. Isomerization of 1-methylindene in a medium containing deuterium oxide showed a very small hydrogen exchange as compared to the rate of isomerization. Such observations were concluded to be inconsistent with a stepwise mechanism involving the formation of a mesomeric carbanion which is subsequently protonated by the conjugate acid of the basic catalyst. Protonation of the methylindenyl anion exclusively in the unsubstituted position was believed to be unlikely. A concerted mechanism could be excluded since the reaction medium contained no protonating agents which could attack the indene at the same time as did the base.

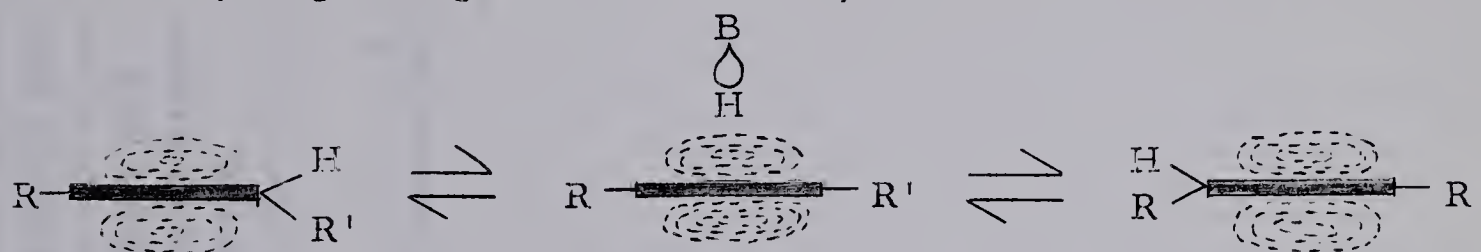
The above considerations led to the proposal of a second mechanism, an intramolecular proton transfer from the 1- to the 3-position, which was also found to be considerably faster than the hydrogen-deuterium exchange. This hydrogen transfer was intramolecular in the sense that it did not involve participation of protons from the medium; i.e. the proton in the 1-position of the starting material was identical with the proton in the rearranged product.

Additional kinetic studies by the same workers involving 1-benzylindene, 1-methyl-3-isopropylindene, and 1-methyl-3-tert-butylindene using pyridine solutions of triethylamine, n-butylamine, 1,4-diaza-bicyclo



[2.2.2] octane, and  $\alpha$ -phenylethylamine were undertaken. Some of their results are summarized in Table VI, page 73.

Isomerization of optically active 1-methyl-3-isopropylindene ( $[\alpha]_D = -1.5^\circ$ ) resulted in optically active 1-isopropyl-3-methylindene ( $[\alpha]_D = +1.35^\circ$ ), the rearrangement thus being stereospecific. This stereospecificity suggested that the tautomeric rearrangement involved neither a concerted, nor a stepwise mechanism, but rather a pure intramolecular hydrogen migration, which may be illustrated as follows:



Some of the stereospecificity of the rearrangement was lost however, when DMSO was used as the solvent. Furthermore, when potassium tert-butoxide was taken as the catalyst in tert-butyl alcohol solution, the rate of racemization was much greater than the isomerization rate. These results may perhaps be explained by the presence of a stepwise or concerted mechanism.

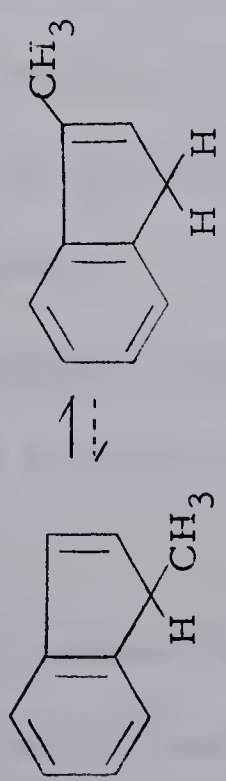
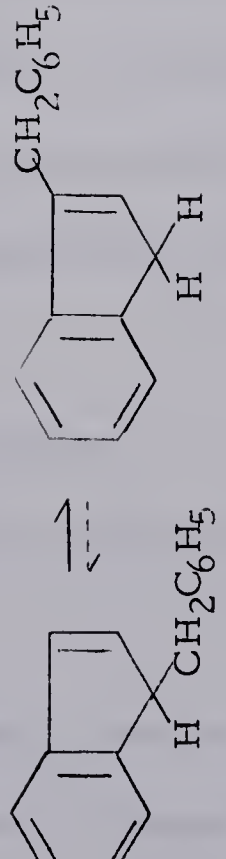
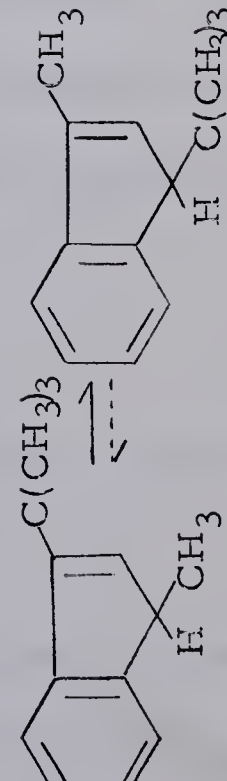
Whether only one mechanism is operative during the isomerizations, or whether more than one participate at the same time can perhaps not be fully concluded. Our results on the thermal rearrangement of 1-methylindene do not disagree with the intramolecular hydrogen shift.

Noteworthy is the fact that no isomerization whatsoever occurred when a solution of 1-methylindene in DME containing 6N hydrochloric acid



TABLE VI

Base-catalyzed rearrangement of 1-substituted indenenes in pyridine solution at 30°C  
(Results taken from the work by Bergson and Weidler (41))

$A \xrightleftharpoons[k_{-1}]{k_1} B$		Conc. of A M	Amount of A in equilibrium mixture	Catalyst Conc. of catalyst M	$k \times 10^{-4} \text{ sec}^{-1}$ pseudo-first order
	$\rightleftharpoons$	2.0	not measurable	$\text{N}(\text{C}_2\text{H}_5)_3$	3.0
		2.0	"	"	1.5
	$\rightleftharpoons$	---	"	"	4.6
		---	"	"	0.36
	$\rightleftharpoons$	---	"	$n\text{-C}_4\text{H}_9\text{NH}_2$	0.36
		0.5	20%	"	1.47 ( $k_1 + k_{-1}$ )



was stirred and refluxed for 1.5 hours. Bergson and Weidler (41), as well as Cristol and co-workers (101) reported similar observations. Contact with strong acidic reagents ( $\text{AlCl}_3$ ,  $\text{H}_3\text{PO}_4/\text{P}_2\text{O}_5$ ) did cause an immediate and quantitative formation of a polymeric product (101).

5. Dimethylindene (both 1,1- and 1,3-dimethylindene) was produced in both cases when the metalated indene, obtained from the reaction of equivalent quantities of metal and indene, was treated as usual with a 50% excess of methyl iodide. Under the conditions used, somewhat more dimethylindene was obtained from 1-indenylpotassium (12-16%) than from 1-indenyllithium (11-13%).

About 15-25% of the dimethylindene was the 1,1-dimethyl isomer. This rose to 33% when the metalated indene was prepared by heating an excess of potassium with indene for 20 hours. But generally, long or short periods of reflux during metalation with an equivalent quantity of metal and indene did not change this proportion (15-25%) much. Furthermore, from the results in Table II, no clear indication exists of the effect of temperature during methylation on the proportion of 1,1-dimethylindene to 1,3-dimethylindene.

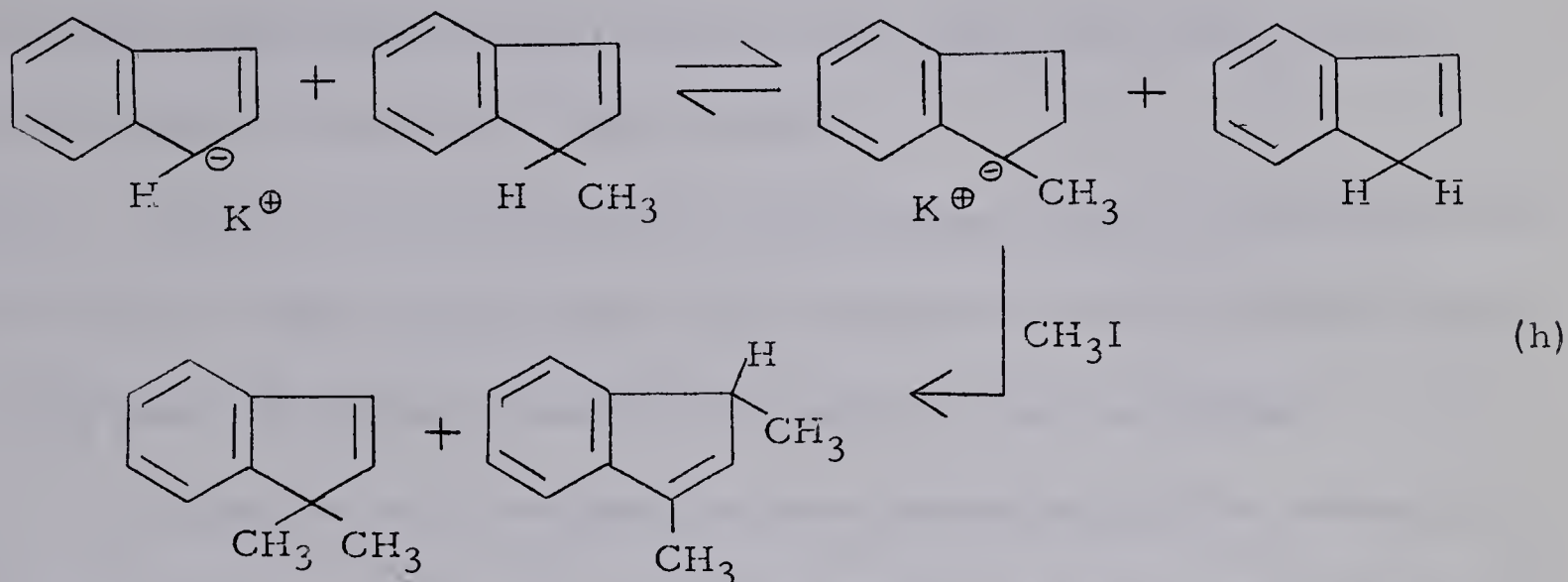
#### Possible routes leading to dimethylindenes

There are a number of ways by which dimethylindenes could be formed.

(i) One route could be via a metal exchange reaction such as that shown in equation (h) in which, for example, the newly formed 1-methylindene could

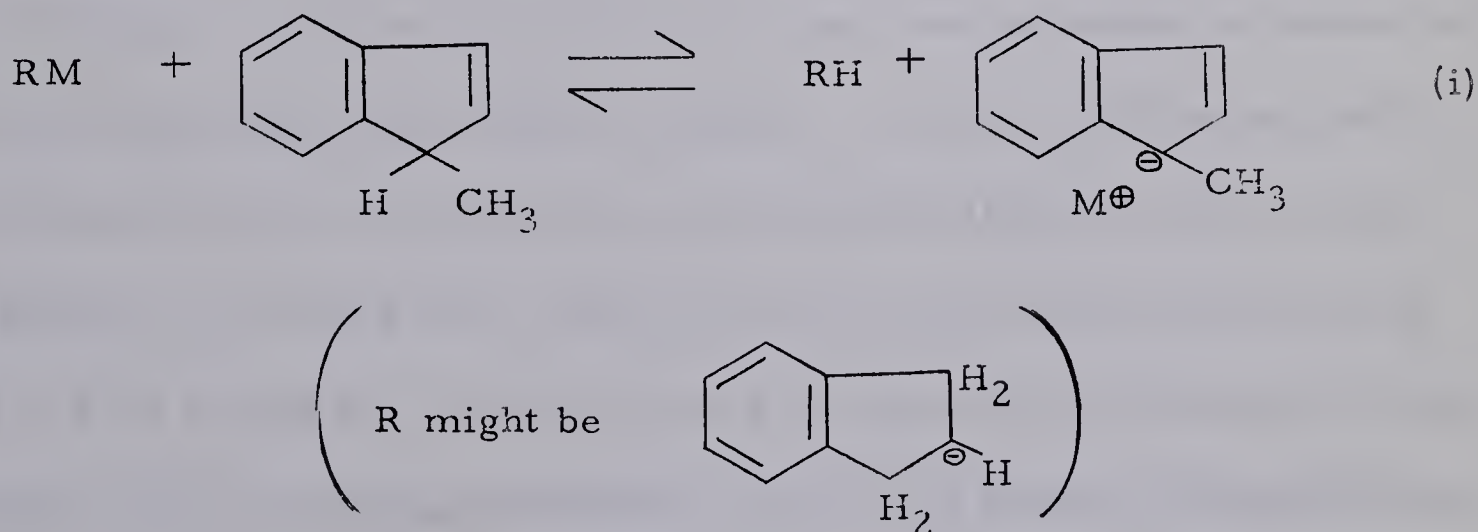


react with 1-indenylpotassium to form indene and 1-methyl-1-indenylpotassium. The latter substance would then react with methyl iodide to



give both 1,1-dimethylindene and 1,3-dimethylindene. Obviously, a similar exchange reaction could occur between 1-indenylpotassium and 3-methylindene, leading to the formation of the same products.

(ii) A second route might be by reaction of the monomethylindene with residual metal adduct according to equation (i), yielding both reduced material (e.g. indan) and metalated 1-methylindene.



(iii) A third pathway to the dimethylindene could be due to the presence, during the methylation step, of unremoved unreacted metal. This, either



by direct reaction with methylindene accompanied by hydrogen evolution , or by prior formation of a metal adduct with the 1-methylindene or liberated indene followed by reaction of the adduct with methylindene , would produce metalated 1-methylindene .

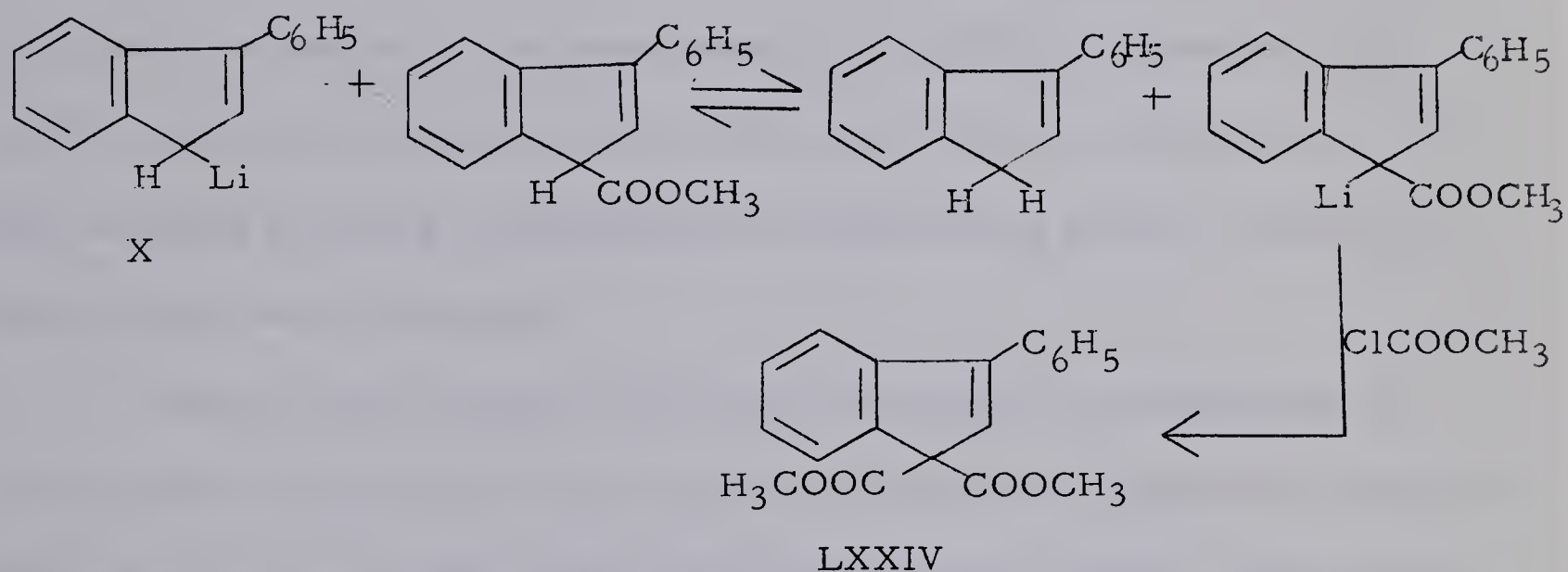
(iv) Finally , it is also possible that prolonged reflux of the metal with the solvent , DME , might produce basic materials which could then readily bring about alkylation of methylindene and the liberated indene .

In support of the exchange process (equation h) is the recovery of substantial amounts of indene from the methylation reactions . That all of the indene had originally reacted with the metal during metalation (equations e and f) is indicated by the similarity of results obtained from both short and long metalation periods . Incomplete reaction of metalated indene with methyl iodide was ruled out since the color of the indenyl carbanion rapidly disappeared upon addition of the methyl iodide . Accordingly , the recovered indene most likely arose from a reaction such as that in equation (h) . However , equation (h) predicts that one mole of indene is regenerated for each mole of dimethylindene produced . It was actually observed for the lithium salt that the ratio of indene to dimethylindene in the product was between 7/13 and 10/12 , while for the potassium salt this ratio was 8/16 to 8/12 (Table II) . In fact , when a 2:1 proportion of potassium metal to indene was used during metalation , the ratio of indene to dimethylindene was only 2/19 .

Work has appeared in the literature both for and against the exchange

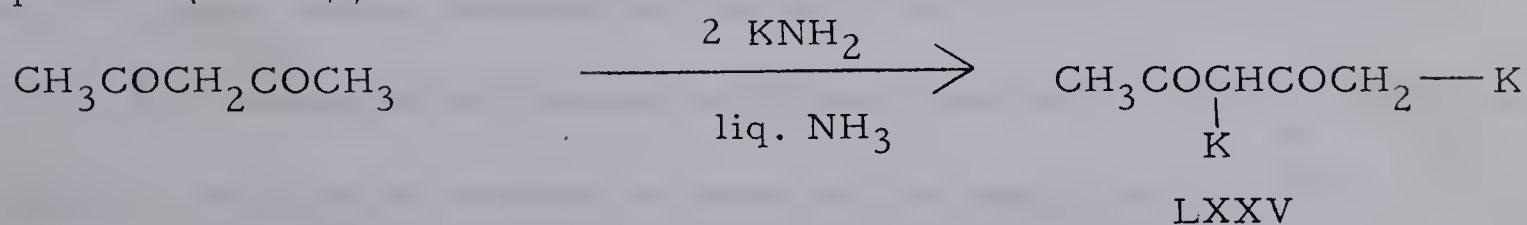


reaction illustrated by equation (h). In support of the exchange reaction O. Blum-Bergmann (22) noted that when 3-phenyl-1-indenyllithium (X) was shaken with methyl chloroformate, the expected 3-phenylindene-1-carboxylic acid methyl ester was not isolated. Instead the diester, 3-phenyl-1,1-dicarbomethoxyindene (LXXIV) was obtained. Obviously the first-formed monoester must have undergone an exchange reaction with more of the indenyllithium, since a nearly theoretical amount of 3-phenylindene was

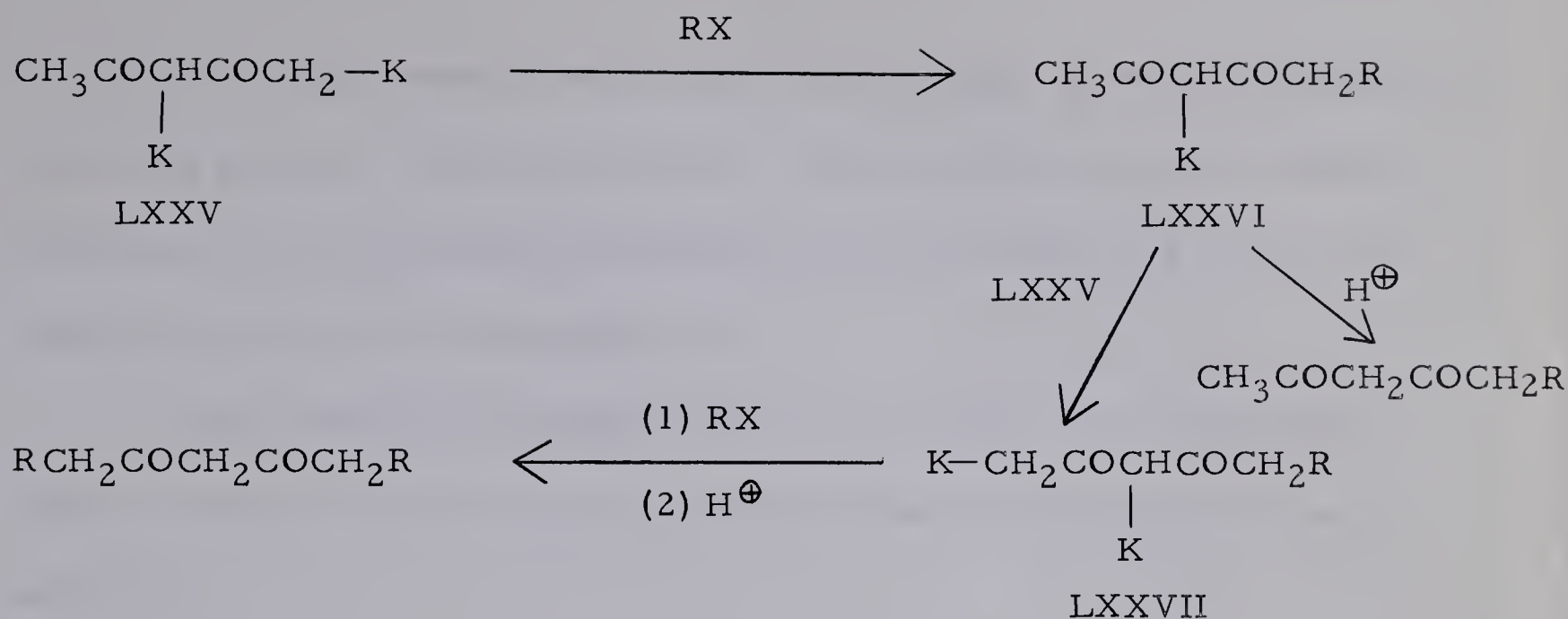


recovered. A similar reasoning has been offered for the dimethylation of 9-fluorenyllithium (22).

Hauser and co-workers(104) have shown definite evidence for an exchange reaction like that in equation (h). Alkylation of the dipotassium salt of acetylacetone using one (or even less than one) equivalent of alkyl halide in liquid ammonia, not only resulted in fair to good yields (35-57%) of mono-alkylated product, but also substantial amounts of the 1,5-dialkylated product (14-26%).







The partial conversion of the monopotassio salt LXXVI to dipotassio salt LXXVII, effected by dipotassio salt LXXV, was clearly demonstrated. No such exchange resulting in dialkylation was noted when disodio- and dilithio-acetylacetone were employed.

Dressler and Kurland (105) have reported the cyanoethylation of excess indene using catalytic quantities of benzyltrimethylammonium chloride-KOH as the base as yielding only 3-indenepropionitrile (38%). With excess acrylonitrile only polycyanoethylated indenenes were isolated, namely 1,1-indene-dipropionitrile (20-25%) and 1,1,3-indenetripionitrile (70%). By varying the experimental conditions therefore, mono- or polyalkylated indenenes can be obtained. However, due to the lack of information concerning product analysis, no conclusive evidence either for or against an exchange route is available. Noteworthy is the fact that no 1,3-disubstituted indene was obtained.

Lansbury and Thedford (106) on the other hand considered acid-base equilibrations rather unimportant in determining product distributions. Following metalation of fluorene by lithium aluminum hydride in pyridine solution, benzylation resulted in considerable quantities (26-47%) of 9,9-di-



benzylfluorene only when excess hydride was present, or when benzyl chloride was added slowly to 9-fluorenyllithium. Rapid addition, inverse addition, or the absence of excess base only resulted in the formation of a mixture of starting material and 9-benzylfluorene.

Even though an exchange route is very likely, our results also indicate that it is not the only way in which dimethylation of indene can be achieved.

The second route suggested (equation i), involving the presence of residual metal adduct, appears unlikely since the formation of 2-methylindan, the product of the reaction of methyl iodide with 2-indanyllithium, should be expected if significant amounts of the residual metal adduct were present. Careful GLC analysis failed to reveal any methylated indans. However, the presence of more complicated metal adduct structures which could cause reaction such as equation (i) and themselves be non-detectable upon work-up by GLC cannot be ruled out.

That the presence of unreacted metal does increase the proportion of dimethylated product has been shown previously when equivalent amounts of potassium and fluorene were allowed to react only for a limited time so that much unreacted metal was visibly present. Methylation of this mixture gave a higher proportion of 9,9-dimethylfluorene than that obtained when the fluorene and potassium had first been allowed to react much more fully (30). In the present case some of the metal may have dispersed in a finely divided state and thus was not removed. This is more likely with potassium than



with lithium since at the reflux temperature of DME, potassium was molten and thus could be dispersed, while lithium remained solid. It was thus more difficult to remove all of the metallic potassium than the metallic lithium. Somewhat more dimethylindene was in fact obtained from the indenylpotassium than from indenyllithium. However, if enough unreacted metal was present to cause the formation of much of the dimethylindene, indicated in Table II, then the formation of metal adducts of not only the regenerated indene but of the monomethylindene is expected, with the latter yielding 1-methylindan. No evidence for the formation of methylindan was obtained, suggesting that substantial amounts of unreacted metal were not present. The fact that from the lithium and potassium reaction roughly similar percentages of dimethylindenes were obtained, and that most if not all of the unreacted lithium metal could be removed, also argues against participation of significant amounts of unreacted metal in the formation of dimethylindenes.

The following experiments bear directly on the question of whether or not unreacted metal was present during the methylation reaction. When 1-indenylpotassium (from 0.1 mole of indene and 0.1 gram-atom of potassium) was isolated, dissolved in fresh DME and the mixture then refluxed with more potassium metal (3.9 g) for 36 hours, only 2.0 g of the metal could be recovered intact. Similarly, when a mixture of 7.8 g (0.2 mole) of potassium in 100 ml of DME containing 0.1 mole of indene was refluxed for 49 hours, it was found that 2.6 g of potassium beyond the equivalent



amount required by the indene had been consumed. That this was not dispersed as finely divided metal was indicated by the insignificant amount of gas evolved ( $H_2 \sim 30$  ml) when water was cautiously added to the resulting cooled residue after as much as possible of the obviously unreacted metal had been removed. These results indicate the possibility that the excess metal was consumed via some type of metal adduct formation which then would undergo a Birch reduction upon addition of water. This "metal adduct" could readily metalate the liberated indene or 1-methylindene during the alkylation step.

The final route to dialkylation suggested above involves reaction of the metal with the solvent to produce basic species. That DME could react with metallic potassium is not unreasonable since it has already been reported that ethereal solvents such as dioxan (107) and aryl ethers (73) are attacked by metal. Coates (71) also makes mention of the fact that ethers are attacked by most organolithium compounds. When potassium metal was heated in refluxing DME for periods of 3, 16.5 and 36 hours, the resulting solutions cooled, and the unreacted metal removed as much as possible, there was clearly visible in each case a nearly colorless precipitate. Filtration gave a solid whose apparently metal-free portion gave a definite basic reaction with pH indicator paper. The filtrate (DME) when refluxed with indene and then treated with excess methyl iodide gave, upon work-up and analysis of the indenenes, recovered unreacted indene containing about 1-2% of methylindene. The alkylindene could have been made



by the reaction of a small amount of dissolved base present in DME since addition of indene to the DME so prepared produced a dark color characteristic of the indenyl carbanion.

When potassium metal (3.9 g) was heated in refluxing DME (100 ml) for 17 hours, the solution cooled and freed as much as possible from unreacted metal, there still remained tiny visible particles of free metal along with the sludge of solid previously noted. Addition of indene to the unfiltered mixture followed by a 1-hour reflux period and then alkylation at 0° as usual gave a product containing 3-4% indan, 62% indene, 4% of 1-methylindene and 31% of 3-methylindene. The source of the indan is clearly from the reductive action of the unremoved metal affording the metal adduct which in turn produced the metalated indene. No doubt part of the metal reacted to produce 1-metal indene and hydrogen. (cf. equations e and f). From the data in Table II, the ratio of indan to the mono- and dimethylindenes was about  $15/(60+15)=15/75$ . It is not unreasonable to assume that in the present case a similar ratio might occur due to the reaction of the metal with indene, and therefore the amount of methylated indene accompanying the formation of 3-4% of indan should be 15-20%. But the actual amount of methylated indene found was 35% of the product. Hence about half of the methylindene arises from some other source-the basic material produced by decomposition of the solvent with the metal.

A similar reaction using lithium metal gave no evidence of methylated



indene or of the decomposition product of the solvent in a reaction with the metal.

It is clear then that the disappearance of so much potassium upon prolonged heating of the excess metal under reflux with indene in DME is very likely due in part to reaction with the solvent, to produce basic products. In an attempt to obtain information as to how DME was affected, the precipitate from a repeat reaction of metal with DME was treated with water and the resulting mixture analyzed by GLC. A peak appeared nearly at the position at which pure  $\text{CH}_3\text{OH}$  registered, suggesting that this alkoxide was present in the decomposition mixture. However, attempts to isolate the material corresponding to this peak on the GLC were unsuccessful.

Scott and co-workers (108) also noticed the decomposition of DME, with possible formation of the methoxide anion. DME was slowly attacked by sodium naphthalene, even at room temperature, with the formation of methyl vinyl ether, presumably in accordance with the following equation, postulated by Scott (108).



Further evidence concerning solvent decomposition was obtained at a later stage of the work reported in this thesis concerning the metalations of acenaphthene. When gases were collected for determination of hydrogen gas content, mass spectrometric analyses also indicated the presence of peaks at  $m/e=15$  and  $27$ , attributable to methane and ethylene. (The



parent peaks at  $m/e=16$  and 28 could not be used due to the presence of atmospheric oxygen and nitrogen in the gas samples). Production of methane and ethylene varying from a few per cent to as much as 20 per cent could be attributed not only to solvent reaction with potassium metal (lithium metal gave no decomposition products), but also very likely to reaction of solvent with the potassium and lithium salts of acenaphthene. Similar views have been expressed by Zweig and Hoffmann (109) when they found that potassium metal adducts of 1,1,4,4-tetraphenylbutatriene were capable of cleaving DME to a considerable extent after 24 hours at reflux temperatures, although not at room temperature.

The above results favor the view that the chief source of dialkylation is via the metal exchange reaction (h). However, some dispersed metal, particularly in the case of potassium, might be present during the alkylation stage and thus would react with liberated indene and methyindene according to equations (e) and/or (f), and thus would form the corresponding metalated indene or methyindene which could then be alkylated. The smaller amount of recoverable indene from that amount expected from equation (h) for the potassium metal reaction than for the lithium metal reaction, is quite likely due to such a reaction with residual metal present during methylation. In addition, potassium's reaction with the solvent DME would supply another source of base which could cause alkylation of both indene and methyindene. Thus the mono- and polymethylated indenenes would form at the expense of the regenerated indene and the monomethyindene.



D. Alkylation of the Product Obtained from Metalation of Indene with Two Equivalents of Metal.

When metalation was accomplished using a molar ratio of metal to indene of 2:1, alkylation produced the results shown in Table VII, page 86. Conclusions drawn from this information can be summarized briefly as follows:

1. When metalation was carried out for short periods (3 hours for potassium, 5-20 hours for lithium) results were nearly identical to those obtained by the use of equivalent amounts of metal and indene (cf. Table II, page 56).
2. With potassium, as the time of metalation was increased, the amount of recoverable indene, as well as the newly-formed monomethylindene decreased, while the quantity of dialkylated and trialkylated indene increased. The quantity of metal consumed was larger for the longer metalation period.
3. With lithium, increase in metalating time gave results about the same as those obtained for shorter metalating periods except that more of the 1-methylindene was isomerized to 3-methylindene.

E. Metalation and Alkylation of Both 3-Methylindene and 1-Methylindene

Equivalent amounts (0.1 mole) of 3-methylindene and metal were heated in refluxing DME (100 ml) for specified times and the cooled solutions freed of unreacted metal and treated with methyl iodide according



TABLE VII

Results of the methylation\* of 1-indenyllithium and 1-indenylpotassium prepared by treatment of indene with two equivalents of the metal

Metal	Time of Used metal- ation, consumed, hours	Amount of metal consumed, %	Reaction products, mole % of total product					Total Recovery %
			Indan Indene	Monomethylation	Dimethylation	Trimethylation	Unknown	
				1-Methyl-3-Methyl- indene	1,1-Di-1,3-Di- methyl- indene	1,1,3-Trimethyl- indene	Products	
Li	5	~40	9	47	1	8	0	0
**	19	~40	10	57	trace	6	0	trace
			8	47	trace	5	0	trace
	20	35-40	10	46	1	9	0	0
	72	45-50	10	34	2	12	0	0
K	3	~45	16	0	3	12	2	1
	3	~48	15	0	2	11	1	0
	20	~60	16	0	5	14	8	1
	20	~65	17	0	5	18	9	0
	46	~80	19	0	8	19	13	1
**	63	~75	20	0	7	21	15	1
			16	0	5	15	9	1
	92	~80	17	0	7	21	18	0

\* Methylation was done at 0°C.

\*\* In these two cases a material balance was made to estimate total recovery, using tert-butylbenzene as an internal standard. The upper line of figures represents the percentages of each substance based on the total amount of isolated product. The lower line is the percentage of each product based upon the indene originally used.



to the procedures used for indene itself. The results are compiled in Table VIII, page 88. Similar reactions were done using 1-methylindene and these results are given in Table IX, page 89. Comparison of the information shown in these Tables with those for the analogous reactions involving indene (Table II, page 56) lead to the following conclusions.

1. As for the reactions of metal with indene, long or short reflux time during metalation produced results which were nearly identical with each other, except that for potassium metal, somewhat more trialkylated indene was formed when the longer reflux time for metalation was used.
2. Total recovery from the metalation and alkylations of the 1-methylindene was 95% when potassium was used, and 98% for the lithium reactions. These are substantially higher than those obtained for the analogous reactions using indene.
3. A substantial proportion of the product was the reduced form, 1-methylindan. This was greater (total of 22-27%) than the proportion of indan found from reactions involving indene (8-17%) (Table II).
4. For lithium, the total amount of monoalkylation of methylindene ( $\sim 70\%$  of product) was about the same as the proportion of monoalkylation of indene, while the dialkylation of methylindene to produce 1,1,3-trimethylindene was much less (about 2 to 4% of the product) than that found for indene (about 11-13%). The amount of 1,1,3-trimethylindene from the dialkylation reaction is the same as the amount of recovered monomethylindene, suggesting that dialkylation occurs via the metal exchange route



TABLE VIII

Metalation and subsequent methylation of 3-methylindene in DMF\*

Metal Used	Metalation time, hr.	Metal Consumed, %	Reaction products, mole % of total product					Unknown Products %
			1-Methyl- indan	3-Methyl- indene	Monomethylation 1,1-Di- methyl- indene	Dimethylation 1,3-Di- methyl- indene	1,1,3-Tri- methyl- indene	
Li	17	73-75	23	4	11	58	4	0
	45	~72	23	3	11	59	4	0
K	5	~76	27	18	8	23	24	0
	16	~85	26	16	8	22	28	0

\* For the metalation step, equimolar amounts (0.1 mole) of metal and methylindene were heated in refluxing DMF (100 ml).

Methylation was carried out by adding excess methyl iodide to the above solution, first cooled to 0°.



TABLE IX

Metalation and subsequent methylation of 1-methylindene in DME\*

Metal Used	Metal- ation time, hr.	Metal con- sumed, %	Reaction products, mole % of total product				Unknown Products %	Total Recovery %
			1-Methyl- indene	3-Methyl- indene	Monomethylation 1,1-Di- methyl- indene	Dimethylation 1,1,3-Trimethyl- indene		
Li	16	~82	22	0	11	61	3	0
	46	~92	24	0	11	61	2	0
**			27	0	10	57	2	98
K	16	~87	24	0	9	21	29	0
	5	~84	23	0	9	23	27	0
**			27	0	8	21	23	95

\* In the metalation step, equimolar amounts (0.1 mole) of metal and methylindene were heated in refluxing DME (100 ml). Methylation was carried out by adding excess methyl iodide to the above solution, first cooled to 0°.

\*\* These figures represent a material balance using tert-butylbenzene as an internal standard. The % yields are based upon the original amount of methylindene used. The line of figures immediately above are for the same run and represent the yield of each product as a % of the total product.



shown by equation (h).

5. With potassium, the amount of monoalkylation (to dimethylindene) is about 30% of the product whereas similar monoalkylation of indene gave about 60% of the product as the monomethylindene. However, the 1,1,3-trimethylindene (from dialkylation) occurred to the extent of 24-29% while recovered unalkylated monomethylindene was found to the extent of 16-18% of the product, indicating that other routes as well as that of metal exchange, brought about dialkylation.

6. Results of the reactions with 1-methylindene (Table IX) and 3-methylindene (Table VIII) are nearly identical. The only significant differences are the slightly higher amounts of metal consumed by the reaction with 1-methylindene, and the recovery of only 3-methylindene rather than the original 1-methylindene as "starting material" (Table IX).

## Part II - Acenaphthene

### Metalation of Acenaphthene and Alkylation of Metalated Acenaphthene

#### F. The Preparation of Methylacenaphthenes

For reasons similar to those expressed in the indene case, it was felt that in order to study the metalation of acenaphthene and the methylation of metalated acenaphthene, it would be necessary to have authentic samples of the expected products at hand. Analysis by GLC of the products arising from a preliminary experiment involving a reaction between potassium metal



and acenaphthene followed by methylation indicated that metalation did occur quite readily, and that at least eight products were formed. Considering the results obtained from the analogous methylation of metalated indene and 3-methylindene, it was anticipated that the reaction mixture could conceivably contain various reduction and  $C_1$ - $C_2$  alkylated products. Therefore, the syntheses of 2a,3,4,5-tetrahydroacenaphthene, the three isomeric dihydroacenaphthenes, as well as  $C_1$  and  $C_2$  monomethyl- and dimethylacenaphthenes were undertaken. Although formation of the tri- and tetramethylacenaphthenes was expected to be insignificant, the syntheses of 1,1,2-tri- and 1,1,2,2-tetramethylacenaphthene were also included, in order to complete the series.\* The preparative chemistry of these compounds was considered to be of interest in its own right, particularly in the case of the sterically crowded tetramethyl derivative, where the four alkyl substituents are virtually eclipsed.

As mentioned earlier in the Introduction, in order to place substituents at the  $C_1$  and  $C_2$  positions, it would be necessary to proceed via an acenaphthene derivative possessing a functional group at either of these positions. For our purposes it was thought that the preparation of all of the necessary compounds could be most readily achieved by using either the unsubstituted or substituted carbonyl derivative, 1-acenaphthenone.

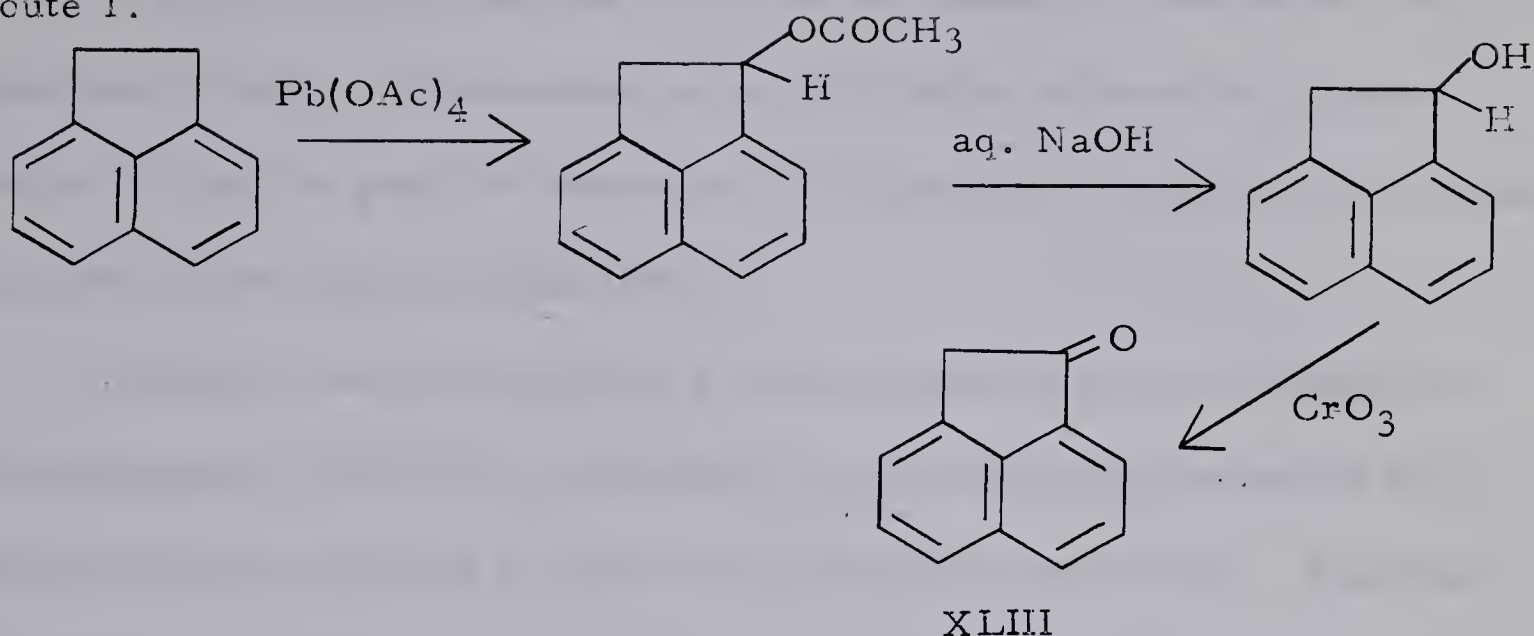
Our preparation of 1-acenaphthenone itself (XLIII) utilized either of the following two methods, shown in the accompanying equations.

---

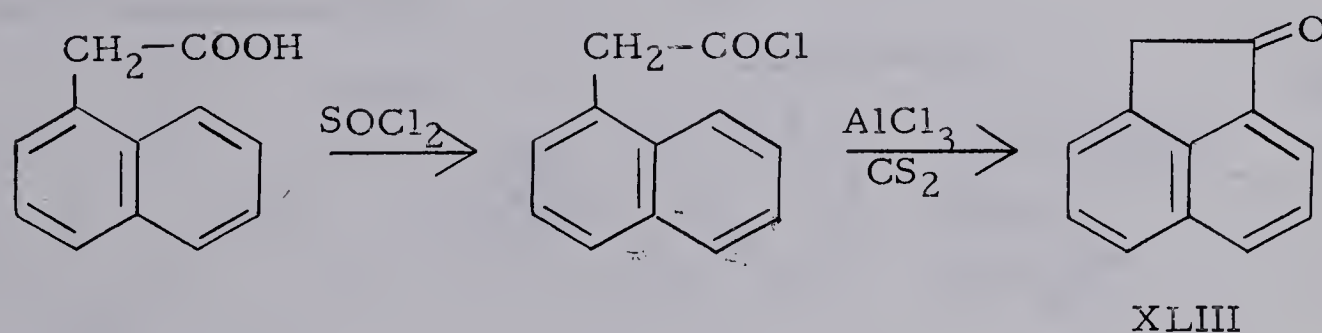
\* Only the  $C_1$  monomethylacenaphthene is reported in the literature.



Route 1.



Route 2.

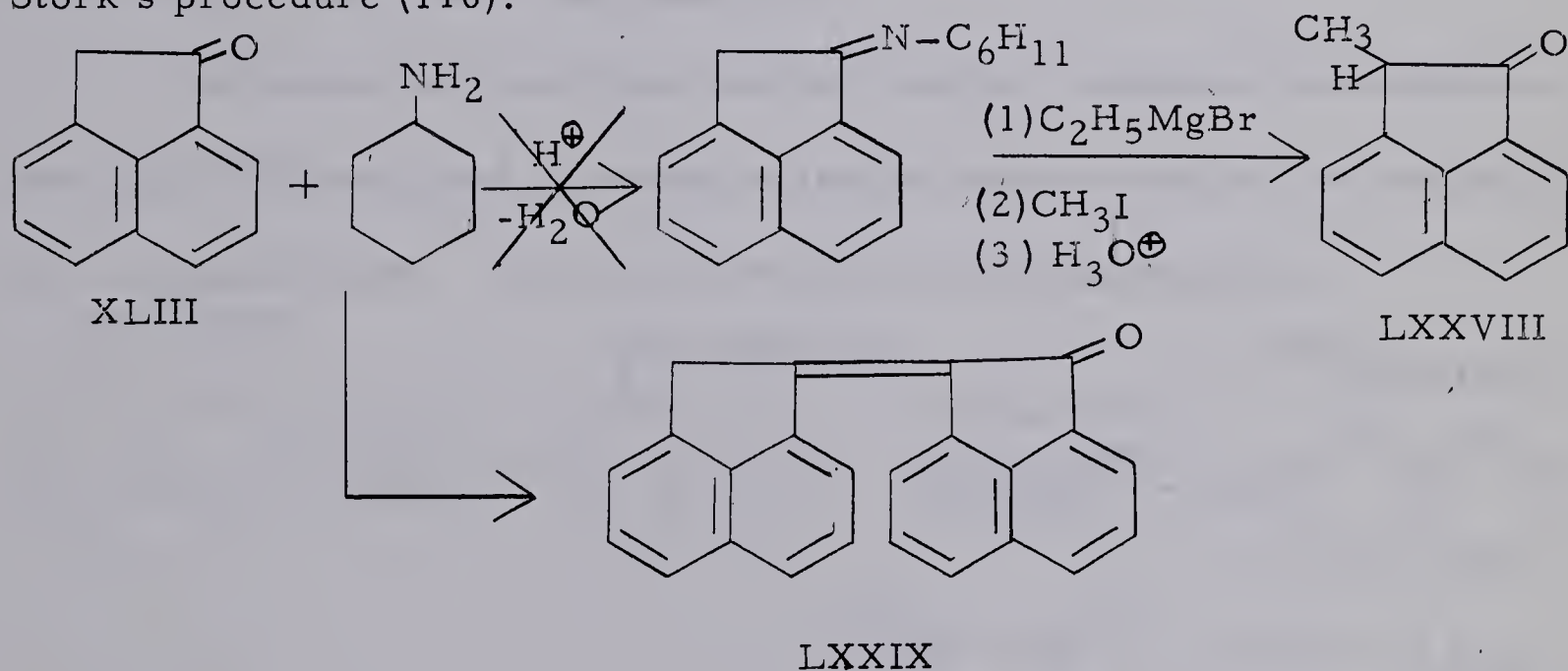


Lead tetraacetate oxidation of acenaphthene (63) resulted in 1-acenaphthenyl acetate, which was easily saponified to 1-acenaphthenol using aqueous sodium hydroxide. The Fieser procedure (63) for the chromic anhydride oxidation of the alcohol gave crude XLIII, containing considerable quantities of chromium salts. Steam distillation of the reaction mixture produced pure ketone, but, via a conventional distillation apparatus, was far too tedious, requiring large volumes of distillate. A more convenient purification involved removal of the chromium ions by cold aqueous sodium hydroxide wash of benzene solutions of the crude acenaphthenone. This procedure, after final work-up, gave a 46% yield of good quality 1-acenaphthenone.



A much simpler method employed commercially available 1-naphthaleneacetic acid. Conversion to the acid halide followed by Friedel-Crafts cyclization gave the ketone in 60-70% yields. Small-scale cyclizations resulted in even higher yields (84%).

The first attempt to prepare the monomethyl ketone, 2-methyl-1-acenaphthenone (LXXVIII) is outlined in the accompanying equation and involved the formation of N-cyclohexylacenaphthenone imine. This was expected to undergo methylation, after proton removal, according to Stork's procedure (110).

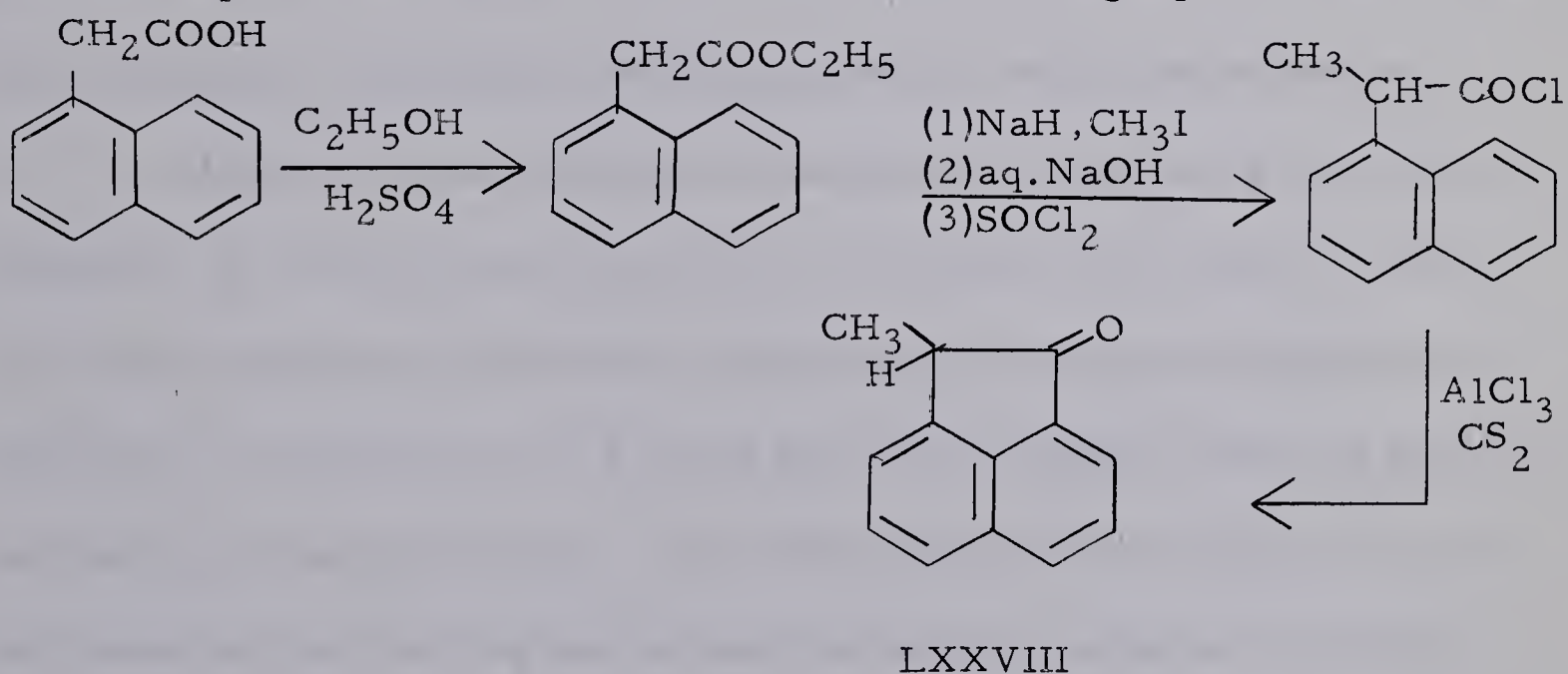


When a benzene solution of 1-acenaphthenone and a slight excess of cyclohexylamine with or without p-toluenesulfonic acid as catalyst was refluxed using a Dean-Stark apparatus (111), a reaction definitely occurred since both water and a yellow precipitate were formed. This precipitate contained no nitrogen, and hence could not be the desired imine. Carbonyl absorption in the infrared at  $1688\text{ cm}^{-1}$  as well as the melting point suggested the formation of biacenone (LXXIX). The melting point ( $269\text{-}270^\circ$ ) was



slightly higher than that reported for biacenone (yellow needles, m.p.  $262^{\circ}$  corr.) (45b), but our elemental analysis agreed with the formulation as biacenone. Since biacenone is readily prepared from XLIII in the presence of base (45b) even at room temperature via an aldol condensation accompanied by water elimination, this is undoubtedly what has occurred in the present case. Even when the experimental conditions were varied, the reaction could not be made to proceed in the desired direction. Only starting material and/or biacenone were obtained as the products. Accordingly, this route was abandoned.

The second and more successful route to 2-methyl-1-acenaphthenone (LXXVIII) employed a procedure similar to that used for the preparation of 1-acenaphthenone. This is shown in the following equation.



1-Naphthaleneacetic acid was esterified by the usual procedure (112) and the ester methylated as described in the literature (113). In our hands however, sodium hydride was found to be a more convenient base than was the reported potassium tert-butoxide (113). An excess of both methyl



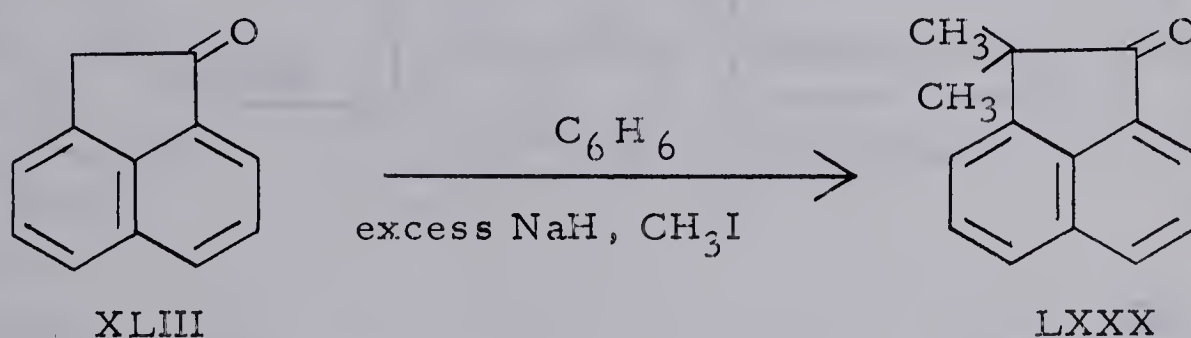
iodide and the base can be used since Julia (113) had shown that only mono-alkylation took place, disubstitution being impossible in this case. The resulting ethyl- $\alpha$ -(1-naphthyl)propionate (93% yield) was readily changed into the acid chloride, which could be cyclized according to the procedure mentioned earlier for 1-naphthaleneacetyl chloride. The resulting dark, sticky organic material obtained from the reaction mixture was found difficult to purify, distillation under reduced pressure being quite unsatisfactory. However, a tedious steam distillation gave a 47% yield of pure LXXVIII as a yellow oil which solidified when cooled. From this, low melting (33-34°) colorless crystals were obtained. It is felt however, that tarring during the cyclization reaction, thus resulting in a low yield, was due mainly to the use of impure, granular aluminum chloride. The use of sublimed aluminum chloride should give much better results.

2-Methyl-1-acenaphthenone was characterized by its elemental analysis, by the NMR and IR spectra, as well as by its oxime. In the infrared spectrum of the oxime a sharp band for hydroxyl appeared at  $3600\text{ cm}^{-1}$ , accompanied by a broad absorption between 3500 and  $3100\text{ cm}^{-1}$  indicating hydrogen bonding. The NMR spectrum of the oxime (Fig. 7) indicated two overlapping sets of methyl-doublets centered at  $\tau=8.32$  ( $J=7$  cps), two sets of methynyl-quartets with the same coupling constant, and two different hydroxyl peaks at  $\tau=1.42$  and  $1.52$ , each existing as a doublet with coupling constant of 1 cps. This clearly indicated the presence of syn and anti isomers, which according to the integrated areas



were present in nearly equal amounts. A broad melting point (126-140°) and the correct elemental analysis added additional support to the view that we were dealing with a mixture of isomers.

Synthesis of 2,2-dimethyl-1-acenaphthenone (LXXX) in 82% yield was readily accomplished by treatment of the parent ketone (XLIII) with excess base and methyl iodide as indicated by the equation below.



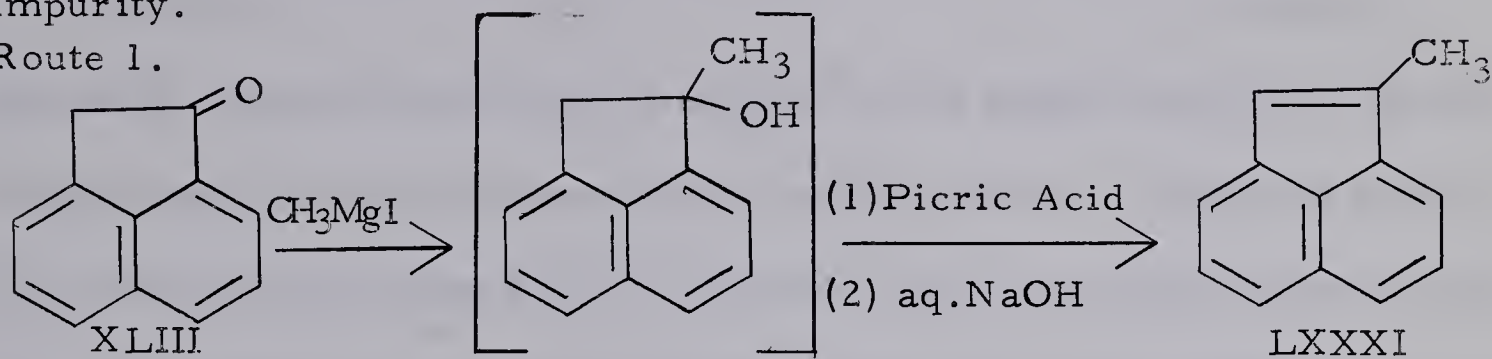
The structure of the pure solid ketone (LXXX) was supported by elemental analysis, NMR and IR spectra. The NMR spectrum (Fig. 8) of the oxime again indicated the presence of two isomers by the appearance of two distinct methyl-singlets, whose integrated areas were in the ratio of 16:84.

From these three ketones (XLIII, LXXVIII and LXXX) a number of methylacenaphthenes could now be prepared. By using the procedure of Brown and Hammick (114) 1-methylacenaphthene (LXXXII) could be prepared. This involved the addition of methylmagnesium iodide to 1-acenaphthenone and gave the expected alcohol, which, without isolation, was dehydrated with picric acid as reported (114). Decomposition of the orange-red picrate with dilute sodium hydroxide solution resulted in the known 1-methylacenaphthylene (LXXXI), isolated as an orange oil (55%).

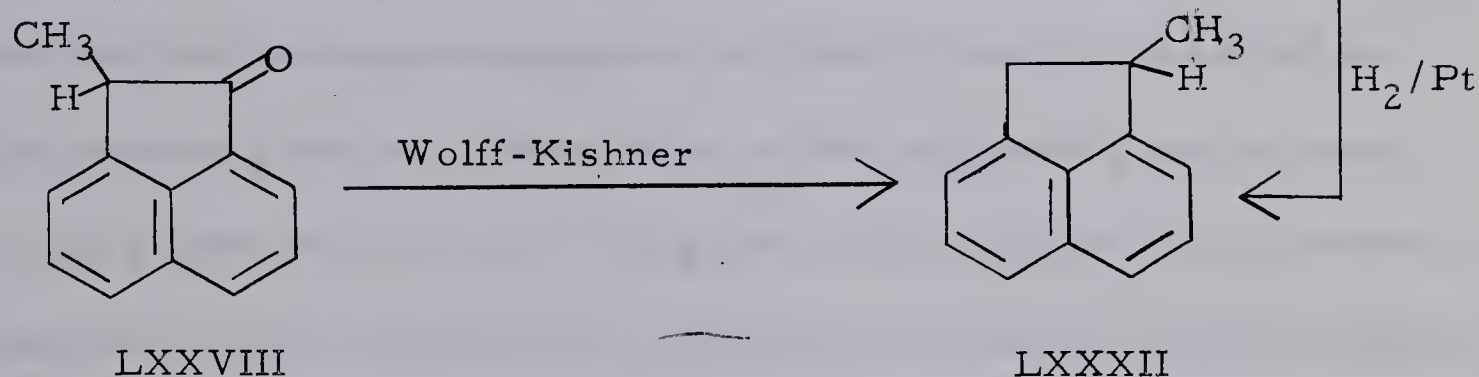


Reduction of the olefinic double bond in LXXXI in ethyl alcohol over platinum catalyst gave an 85% yield of 1-methylacenaphthene as a nearly colorless oil, which yellowed on standing. The physical constants agreed with those reported, but a GLC analysis indicated a 4 to 5% impurity.

Route 1.



Route 2.

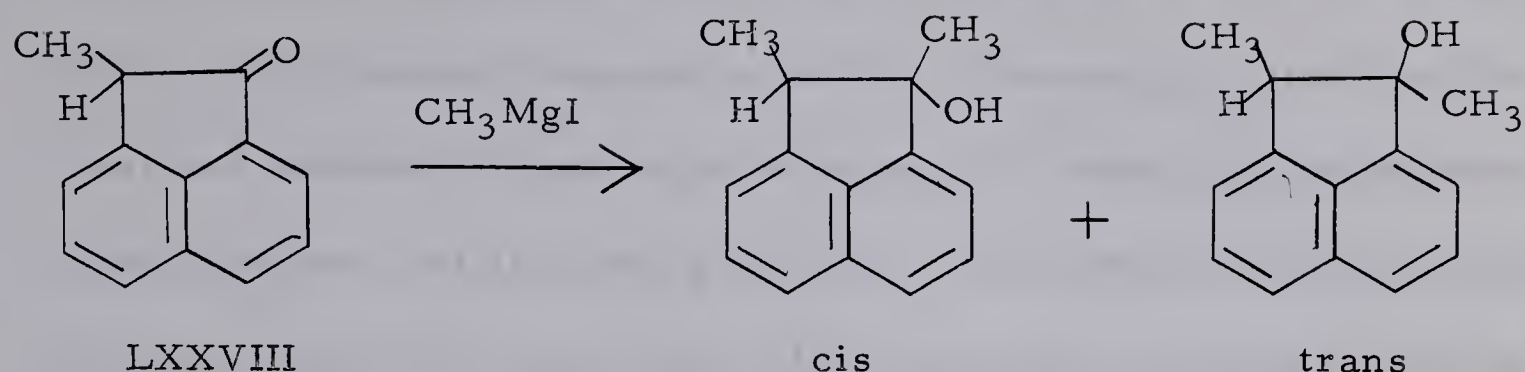


Since the impurity obtained via Route 1 could not be removed, the 1-methylacenaphthene was prepared by a Wolff-Kishner reduction of 2-methyl-1-acenaphthenone as indicated in the above equation. By this procedure (55), using diethylene glycol and potassium hydroxide, pure material was obtained. The NMR spectrum (Fig. 9) corroborated the assigned structure.

In a similar manner, Grignard addition to the functional group of LXXVIII resulted in a 93% yield of 1,2-dimethyl-1-acenaphthenol, as shown in the equation below. Although several recrystallizations gave fine colorless crystals, the melting point range was broad (88-101°), indicative of



cis and trans addition to the keto function.



The NMR spectrum lent further support to the above view (Fig. 10), although the A-60 spectrum was not too well resolved. Analysis of an HR-100 spectrum showed the  $\text{C}_2$ -proton to be a well defined quartet ( $J \simeq 7.3$  cps), with the  $\text{C}_2$ -methyl a doublet having identical splitting. Two additional methyl-singlets appeared at slightly lower field, which is expected due to the deshielding effect of the neighboring oxygen atom. The integrated area ratio of 54:46 points to the fact that the  $\text{C}_2$ -methyl group exerts little influence on the direction of methyl Grignard addition. From the available data however, no definite assignment of configuration can be made.

Dehydration of the mixture of cis and trans alcohols via picrate formation (92%), followed by base decomposition, produced 1,2-dimethyl-acenaphthylene (LXXXIII) as yellow plates. In order to effect cis reduction of the double bond it was thought to make use of the diimide reduction method. The stereochemistry of this reduction has been well established through isotopic labeling experiments, and can also be visualized from the proposed mechanism involving a cyclic transition state (115, 116). This method of hydrogenation has been shown to be more selective than



other methods of reduction, although when steric factors are large it is highly subject to steric approach control. Generating diimide by the catalyzed oxidation of hydrazine did appear to reduce the disubstituted acenaphthylene, but at a very slow rate. Even when the reaction mixture was kept at 45-50° for one week, 43% of the olefin was still present as indicated by GLC retention time. In addition, 13% of an unknown higher-boiling component was also being formed. On the other hand, alternative reduction using hydrogen and platinum occurred very readily at room temperature and 1.5 atmospheres pressure. As was the case with this as well as all the other low-pressure hydrogenations performed in this work, a small amount of a lower-boiling impurity (4-5%) was mixed with the required product. But in this case the oily impurity could be removed from the solid cis-1,2-dimethylacenaphthene (LXXXIV, m.p. 53-54°) by recrystallization of the latter from alcohol. The assumption is made here that the catalytic hydrogenation occurred in a cis manner, an assumption which appears reasonable considering the results reported by van Tamelen and Timmons (117).

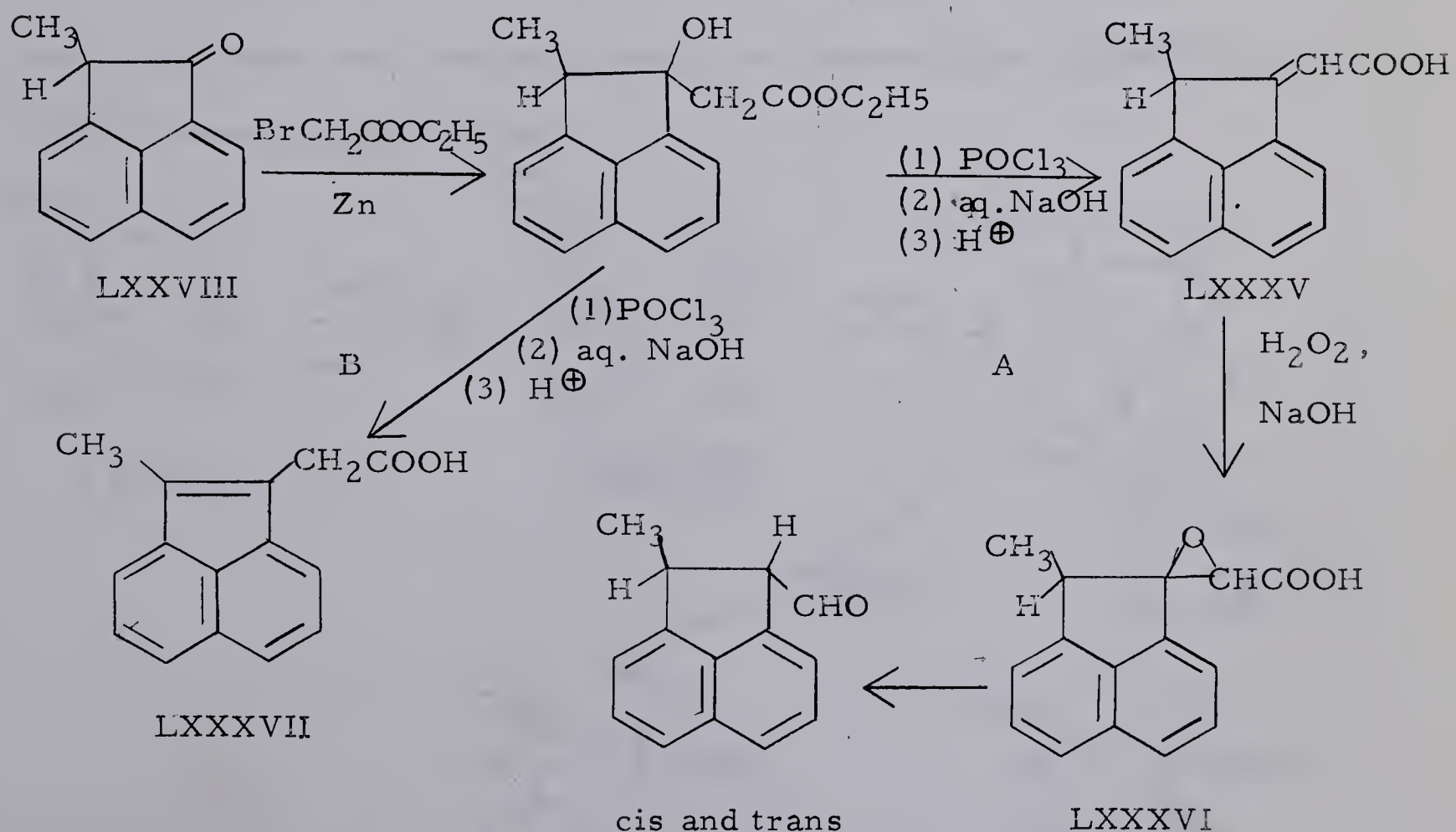
The NMR spectrum (Fig. 11) of compound LXXXIV is reasonable for the structure of cis-1,2-dimethylacenaphthene, but shows some interesting aspects. The two identical methynyl protons appear as a sextet centered at  $\tau = 6.26$ , though with different coupling values between the various peaks ( $\tau \simeq 5.2-7.0$  cps). The two equivalent methyl substituents however, do not show up as the expected doublet. Rather, here also six peaks are



visible, all of which are real. Obviously, first-order approximations are not applicable in this case.

Synthesis of the corresponding trans-1,2-dimethylacenaphthene was unsuccessful, though a number of attempts were made. Since in the acenaphthylenes cis and trans isomers do not occur, a route through this olefin was excluded; one could anticipate considerable difficulty therefore in finding a successful synthetic route which would lead to the formation of the pure trans isomer. Initial attempts therefore were made to obtain a cis and trans mixture of some acenaphthene derivative such as an aldehyde or carboxylic acid from which, if separation of isomers were possible, the required methyl groups could be derived.

Scheme A as shown in the following reaction was therefore proposed.

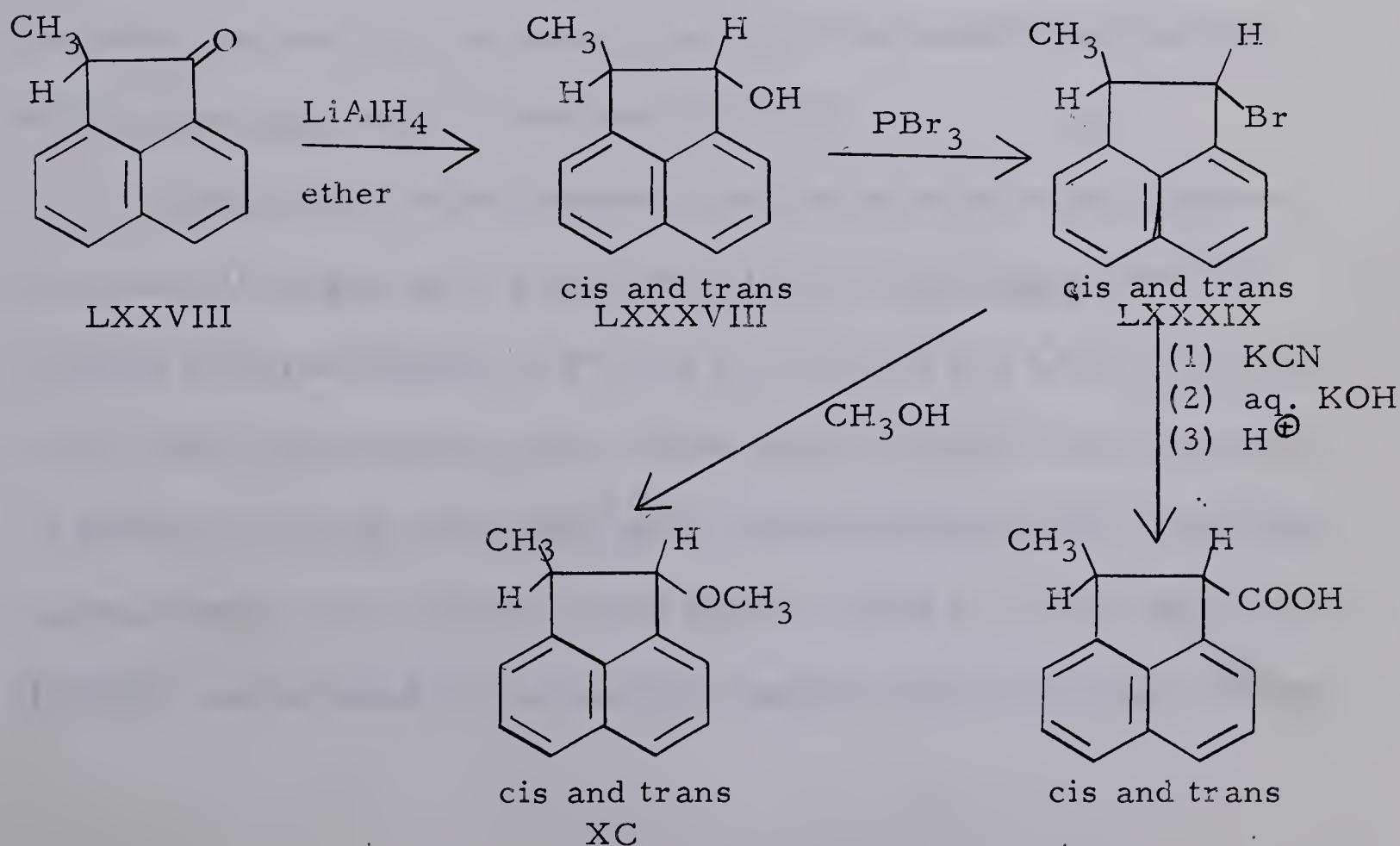




The Reformatsky reaction occurred readily, as did the dehydration and saponification steps. However, the  $\alpha, \beta$ -unsaturated acid (LXXXV) was not obtained. Instead the dehydration reaction followed route B and produced the  $\beta, \gamma$ -unsaturated acid (LXXXVII) as indicated by NMR.

In order to prepare LXXXVI via another route, a Darzens' glycidic ester reaction was thought to be suitable. Avoiding a reaction utilizing ethyl chloroacetate and ethoxide base because of the labile hydrogen remaining on C<sub>2</sub>, the dichloro- or dibromoesters were used instead, in the presence of magnesium amalgam or zinc (118). However the glycidic ester reactions were also unsuccessful since very little reaction occurred (cf. the similar reactions of 1-indanone and related ketones (119)).

Attempts to prepare the carboxylic acid via the route indicated below also were unsuccessful, although the intermediates LXXXVIII and LXXXIX were readily formed.





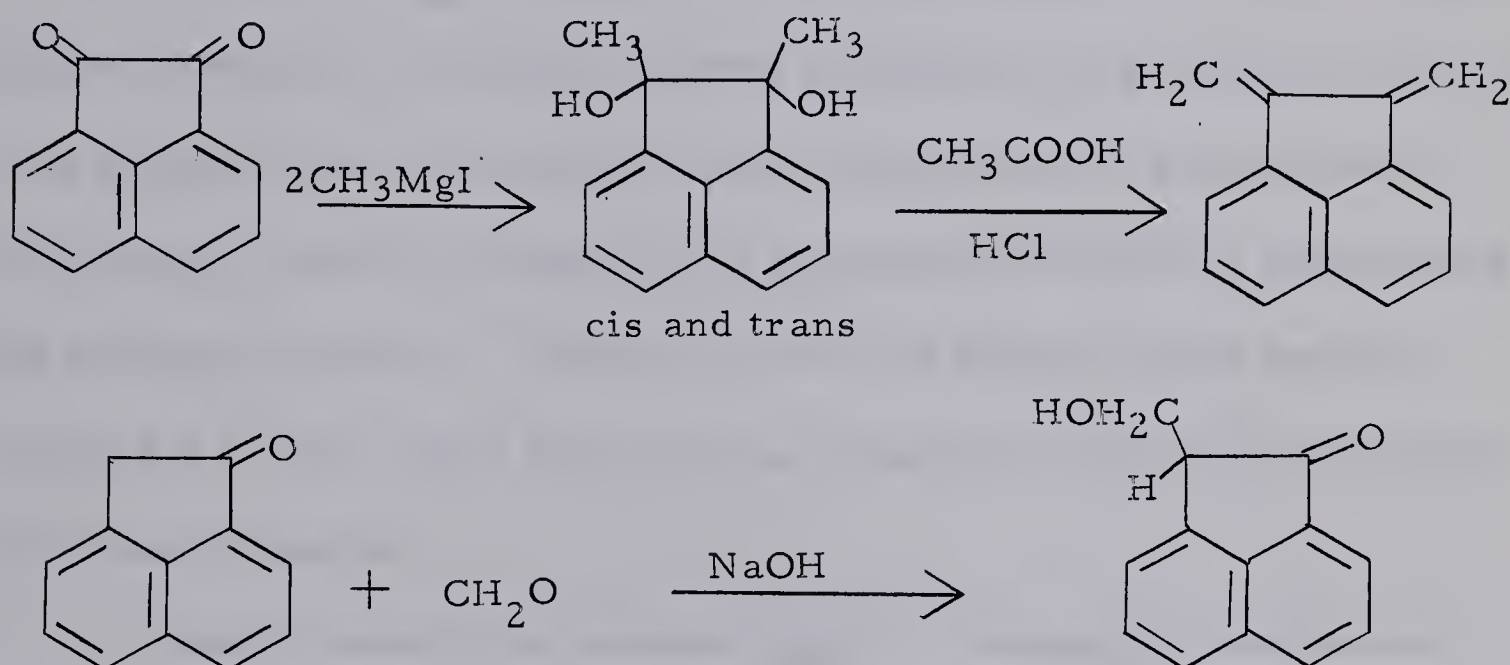
Hydride reduction of ketone LXXVIII resulted in a nearly quantitative yield of a mixture of cis and trans carbinol (LXXXVIII). The NMR spectrum (Fig. 12) proved this beyond doubt, showing two signals for the  $C_1$ -hydrogen, one centered at  $\tau=4.60$  (doublet,  $J=6.5$  cps), the other at  $\tau=4.98$  (doublet,  $J=2$  cps). Dewar and Fahey (120) have observed similar values for the cis- and trans-1-deutero-2-bromoacenaphthene ( $J=7.4$  or  $6.8$ , and  $1.9$  or  $2.7$  cps respectively), which they applied to the Karplus curve (121). The signal having the larger splitting was then assigned to the cis-1-deutero-2-bromoacenaphthene, that with the small coupling to the trans isomer. The dihedral angles corresponding to these coupling values have been reported by Hayward and Csizmadia (59) to be  $\phi_{cis}=18$  or  $24^\circ$  and  $\phi_{trans}=119^\circ$  or  $117^\circ$ . Distortion from the assumed  $\phi_{cis}=0^\circ$  and  $\phi_{trans}=120^\circ$  values expected for fully eclipsed bonds by the bulky bromine atom appears quite reasonable. Similar assignment of configuration on the basis of the observed coupling constants in our work indicated an approximate 45:55 cis to trans ratio of carbinol LXXXVIII.

Replacement of the hydroxyl group by bromine using a general procedure (122) also gave a mixture of isomers (cis:trans  $\simeq 40:60$ ), deduced from the doublets at  $\tau=4.18$  ( $J=7.0$  cps) and  $4.78$  ( $J=3.0$  cps) in the NMR spectrum (Fig. 13). This halide (LXXXIX) lost a molecule of hydrogen bromide extremely easily, and decomposed with concurrent polymerization when attempts were made to distil it. When the bromide LXXXIX was refluxed with potassium cyanide in ethyl alcohol (123), and



the mixture then subjected to potassium hydroxide hydrolysis, it did not yield the desired 2-methyl-1-acenaphthenecarboxylic acid. Warming in methyl alcohol solution similar to the procedure used for 1-bromoacenaphthene (124) did produce a 15-20% yield of cis and trans methyl ether (XC), but gave mainly the olefin (80-85%), 1-methylacenaphthylene (LXXXI).

Two further reactions from which dialdehydes or dicarboxylic acids could be derived were attempted, but both were unsuccessful. These are shown below.



Although both reactions have been reported in the literature (124, 125) the results could not be repeated, probably due to a lack of experimental details found in the literature.

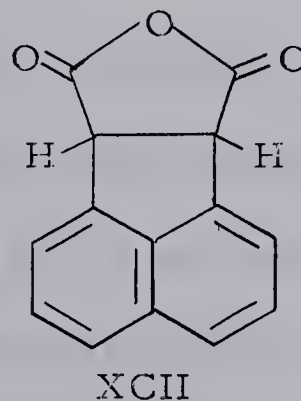
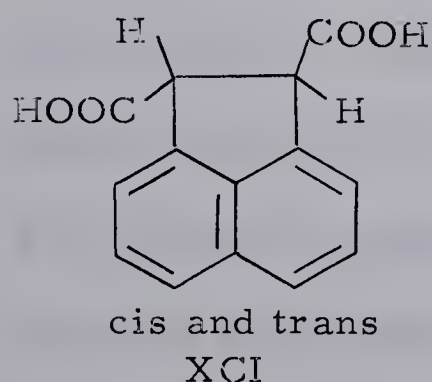
Removal of a proton from cis-1,2-dimethylacenaphthene should result in a planar carbanion which, upon reprotonation during work-up, might lead to a mixture of cis and trans isomers. However, attempts to abstract a proton using n-butyllithium in hexane solution failed, even



though a green-black color, usually indicative of carbanion formation, was observed. Addition of water only regenerated the starting material.

Similar experiments using acenaphthene and n-butyllithium in hexane or hexane-DME solutions, or sodium hydride in DMSO, followed by addition of methyl iodide, gave very little or no alkylation. Here also an instantaneous black coloration was produced when the base was added to the hydrocarbon. In one case when evolved gases were collected, very little butane was detectable by mass spectrometry. These reactions may be compared with those reported by Gilman (65) and Morton (66), who used n-butyllithium and n-amylsodium respectively on acenaphthene. Both groups reported formation of a dicarboxylic acid after carbonating the metalated product. Perhaps in our case better results could be obtained if a more potent base such as potassium hydride-n-butyllithium (126) were employed.

Further attempts to prepare trans-1,2-dimethylacenaphthene were abandoned. It is felt, however, that both cis and trans isomers can be obtained if a 1,2-dicarboxylic acid (XCI) can be synthesized.

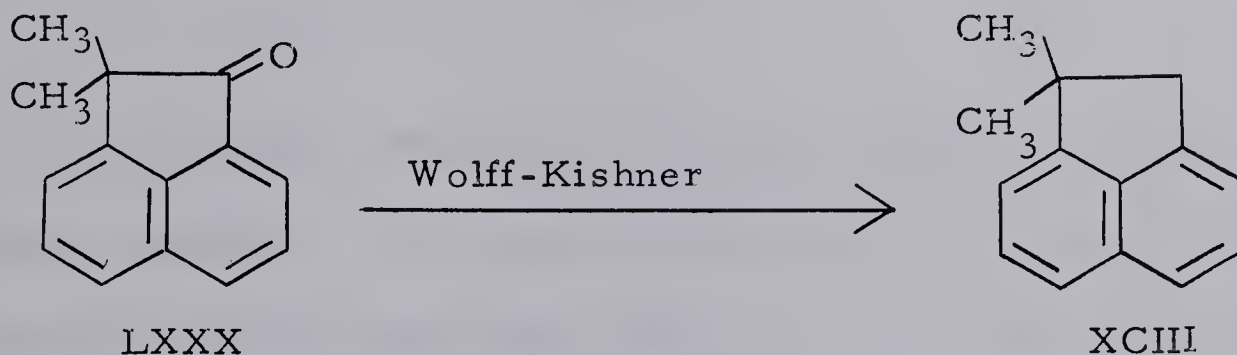


A mixture of such a 1,2-dicarboxylic acid should be separable, since the cis configuration should lend itself to anhydride (XCII) formation,



while the trans would remain as the free acid. A method of this nature should enable one to assign both the cis and trans configurations beyond any doubt. Having both derivatives on hand may also be of interest for theoretical studies. Comparison of the experimental NMR spectra with the theoretical spectra may reveal some effects due to the strained nature of the molecule.

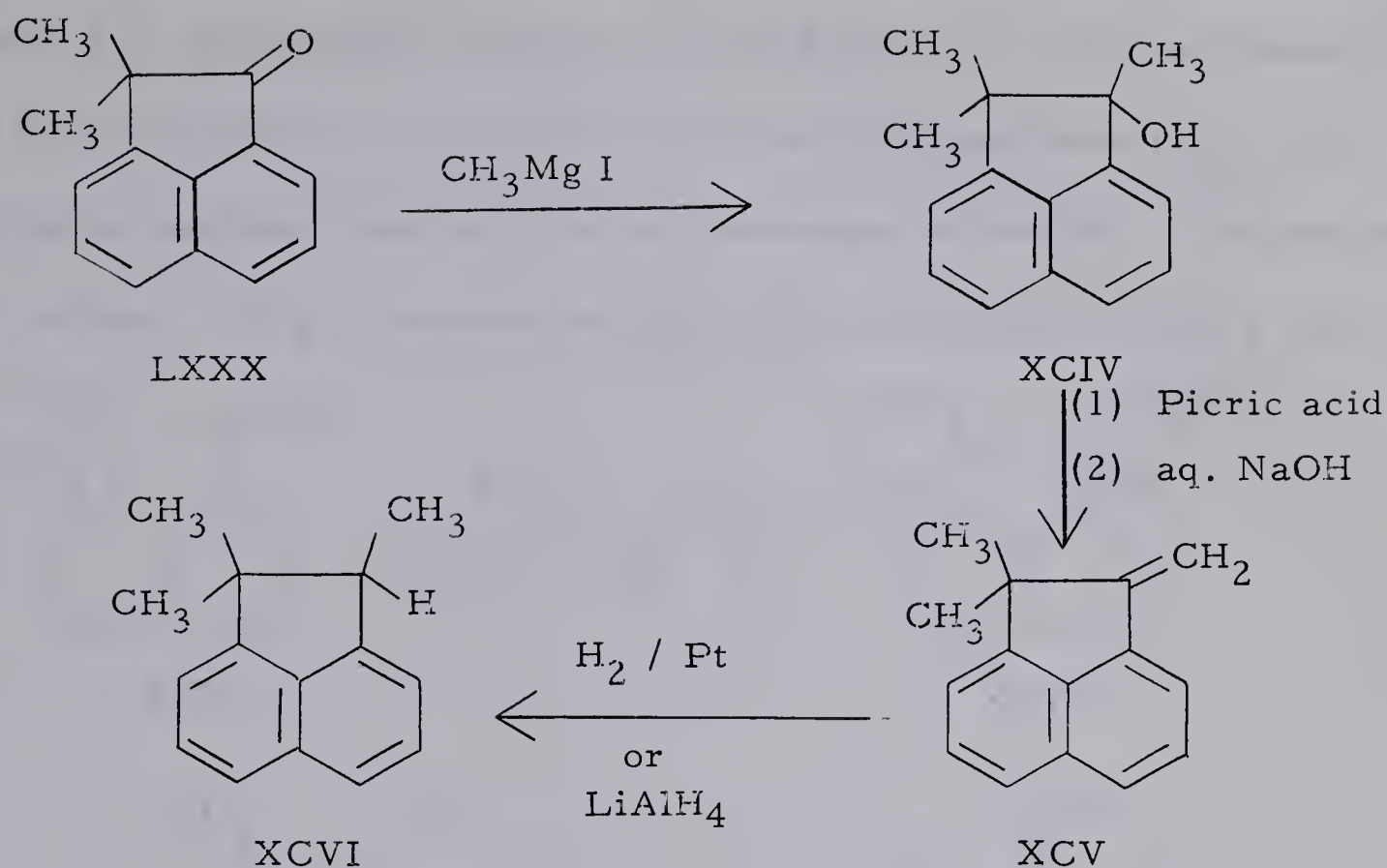
The third dimethyl derivative, namely 1,1-dimethylacenaphthene (XCIII) was readily obtainable from its precursor, 2,2-dimethyl-1-acenaphthenone (LXXX). Wolff-Kishner reduction in the usual manner (55)



furnished the hydrocarbon, characterized by its picrate, in 50% yield.

The ketone LXXX also served as the starting material for the trimethylacenaphthene. Grignard addition to the carbonyl group occurred in nearly quantitative yield with formation of 1,2,2-trimethyl-1-acenaphthenol (XCIV). The NMR spectrum (Fig. 14) agreed with the structure. Dehydration of XCIV with picric acid took place smoothly, affording 2,2-dimethyl-1-methyleneacenaphthene (XCV) as a pale-yellow oil, which darkened on standing. The NMR spectrum (Fig. 15) is in complete agreement with the structure.



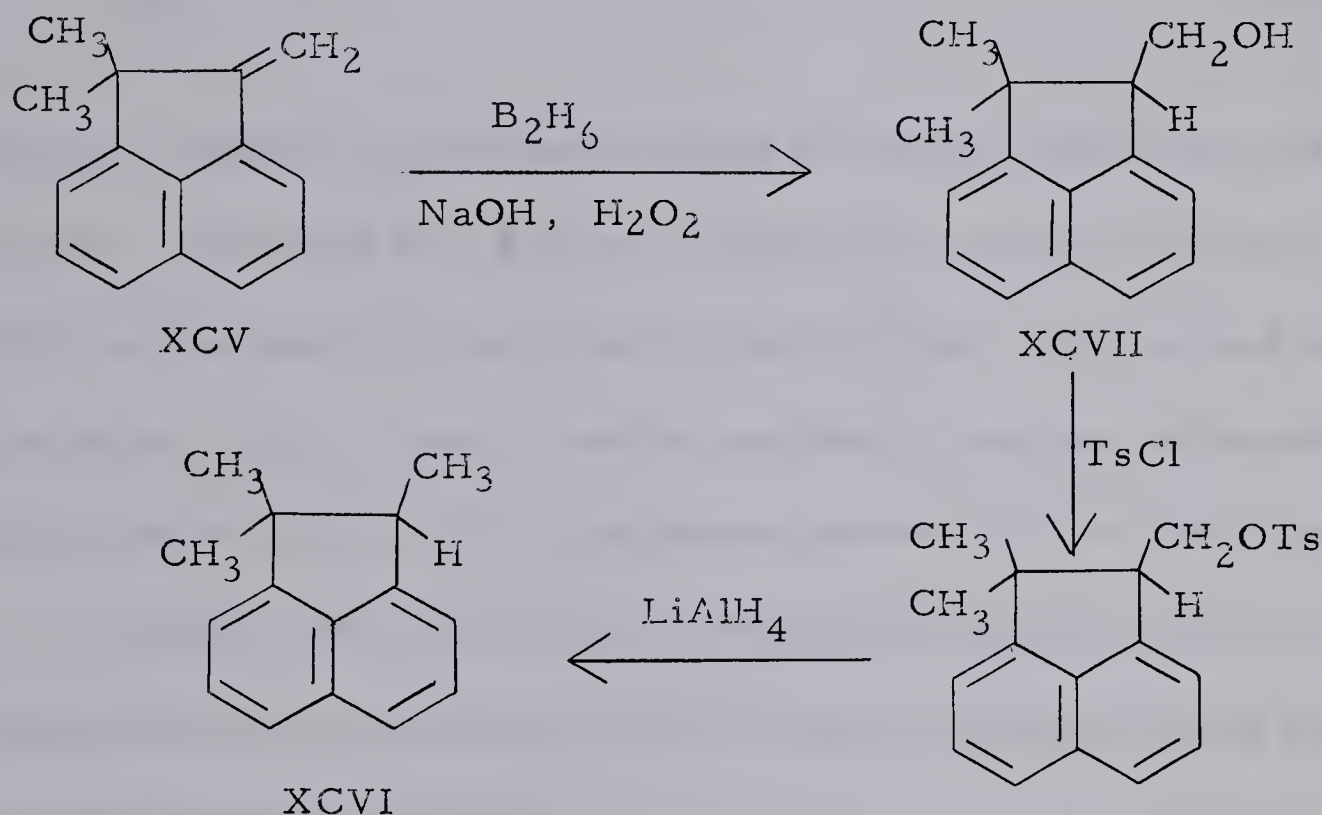


The trimethyl compound (XCVI) was obtained by means of two reduction methods. In the first method, hydrogenation over platinum catalyst reduced the double bond rapidly at room temperature, but gave the final product in only 95% purity. The second method utilized the ability of lithium aluminum hydride to reduce the exo methylene group. After 20 hours reflux in THF solution containing lithium aluminum hydride, only traces of starting material could be found, and XCVI was obtained in good yield in greater than 98% purity as determined by GLC. In both cases, preparative gas chromatography could be used to remove the last traces of impurity.

Another less direct synthesis of 1,1,2-trimethylacenaphthene involved hydroboration of the olefin XCV with sodium borohydride and boron trifluoride etherate in diglyme with subsequent alkaline oxidation (127), and



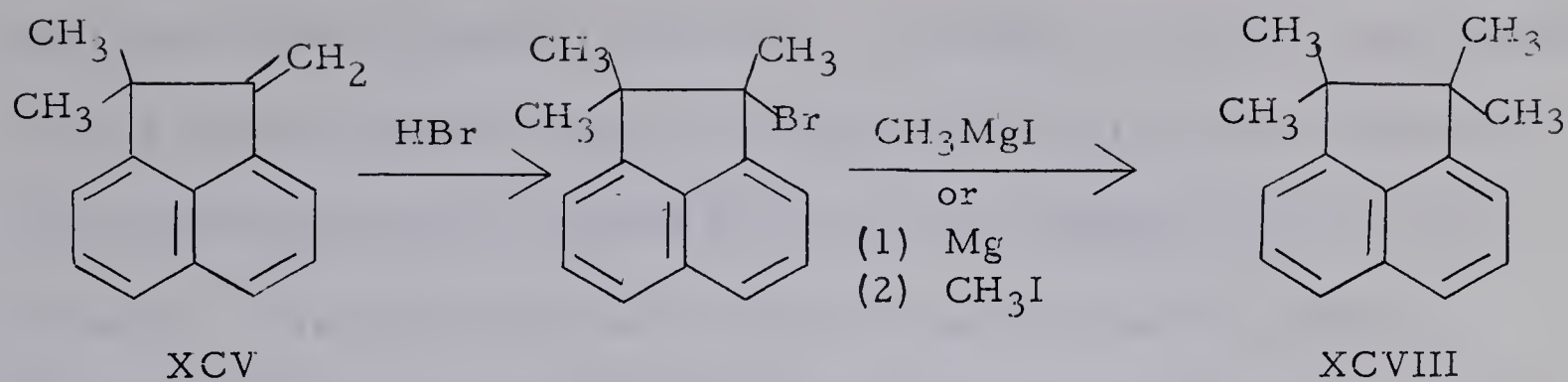
resulted in an extremely viscous oil of 98% purity. This was shown to be the desired primary alcohol (XCVII) by the NMR spectrum (Fig. 16), elemental analysis, and by 3,5-dinitrobenzoate formation. Tosylation of the carbinol with p-toluenesulfonyl chloride in pyridine yielded a solid



p-toluenesulfonate which was quantitatively reduced to 1,1,2-trimethyl-acenaphthene by lithium aluminum hydride in ether solution. The NMR spectrum of this hydrocarbon is shown in Fig. 17.

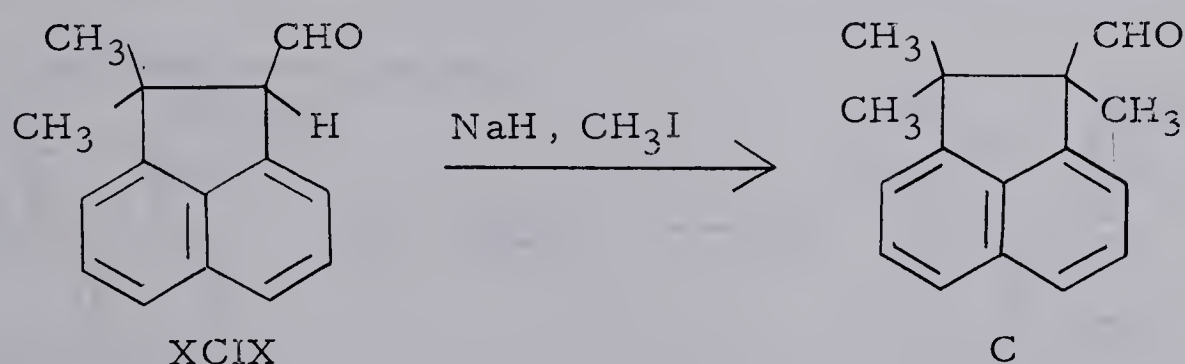
The preparation of the tetramethylacenaphthene was considerably more difficult than that for the trimethyl homologue. The first scheme proposed was that of Markovnikov addition of hydrogen bromide to the double bond of compound XCV, then displacement of the halide by methyl Grignard, or conversion of the halide to the Grignard derivative followed by reaction with methyl iodide according to the equations below.





However, addition of hydrogen bromide to the exo double bond was not achieved. Although the required amount of the halogen acid was added to XCV and appeared to have reacted as required, work-up and attempts at isolation of the tertiary bromide resulted in complete elimination of the halogen acid and nearly quantitative recovery of the starting material.

Attention was then directed towards the preparation of 2,2-dimethyl-1-acenaphthenecarboxaldehyde (XCIX) which in principle could be methylated via a base-catalyzed reaction.

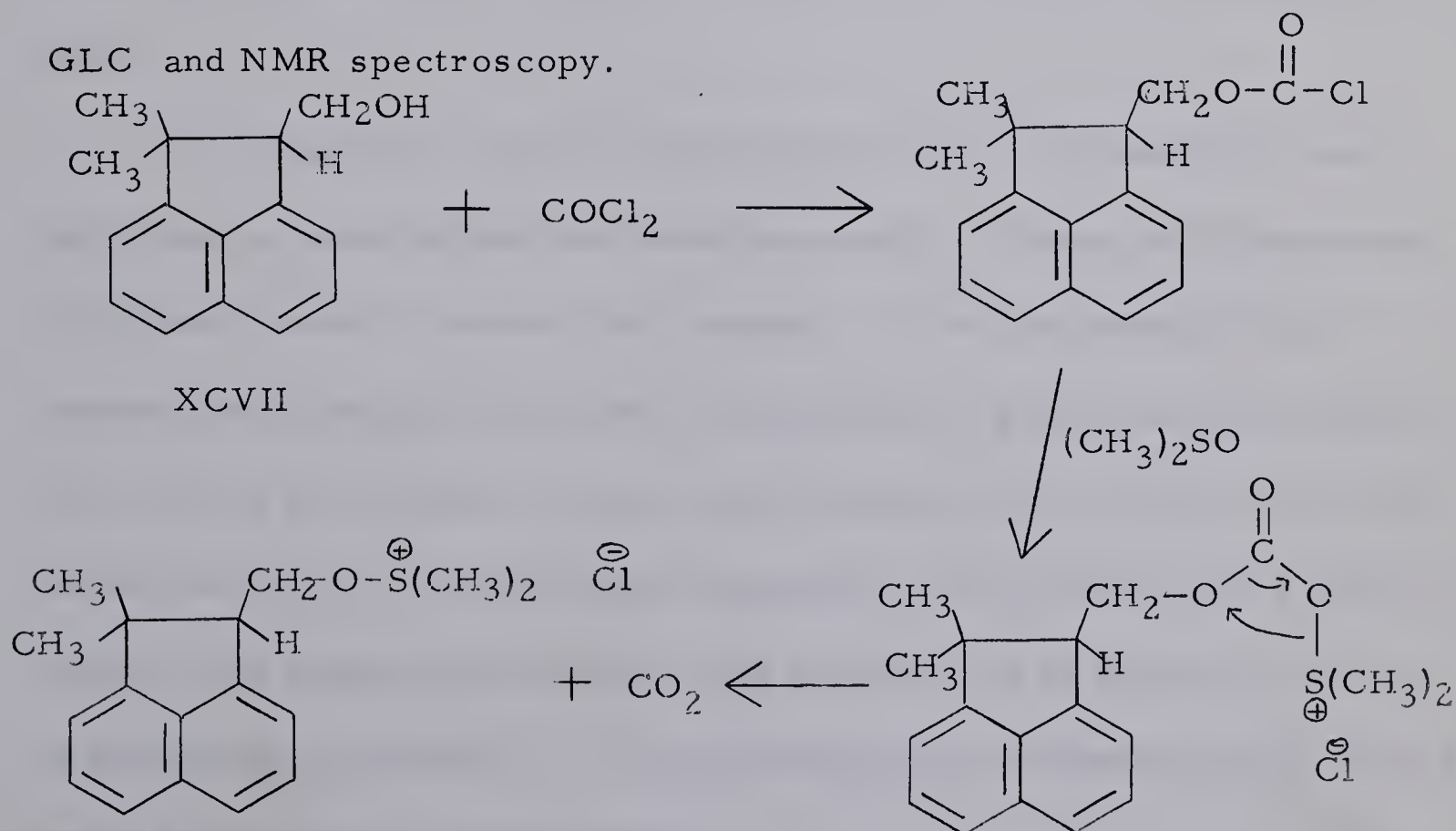


The first attempt to prepare the carboxaldehyde XCIX was by the partial oxidation of 2,2-dimethyl-1-hydroxymethylnaphthalene (XCVII). Oxidations of primary alcohols to the corresponding aldehydes have always been of limited use due to the facile oxidation of the aldehyde to the carboxylic acid. Recent work on the DMSO-sodium carbonate oxidations of bromides and p-toluenesulfonates by Kornblum and co-workers (128) has extended

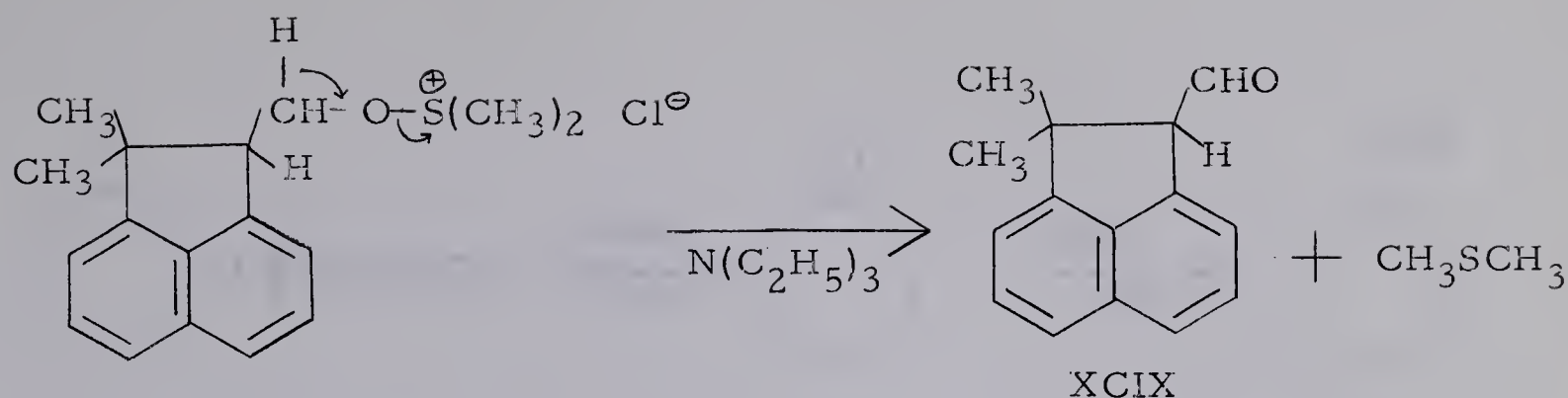


the scope of these reactions somewhat. A similar procedure, also carried out in a neutral medium, has recently appeared (129) in which dimethylsulfoxonium salts were prepared by the action of DMSO on alkyl chloroformates. Vigorous evolution of carbon dioxide occurred, with the formation of an intermediate which, with a slight excess of triethylamine, rapidly gave an aldehyde or ketone and dimethyl sulfide.

Following Barton's procedure (129), the carbinol XCVII was smoothly converted into the chloroformate by an ethereal solution of phosgene. Although it could be isolated and distilled under reduced pressure, the viscous, pale-yellow chloroformate darkened and decomposed on standing at room temperature for prolonged periods of time. Addition of DMSO and triethylamine, followed by the prescribed work-up resulted in a viscous oil which was shown to contain 75-80% of the aldehyde (XCIX) by GLC and NMR spectroscopy.







Purification of the reaction mixture proved to be difficult and tedious, chromatography or sodium bisulfite addition being unsuccessful. However, purification of small quantities by Girard's T reagent could be used, although a large-scale reaction resulted only in tarry decomposition products. It was discovered later however, that decomposition of the reaction mixture was due to the Girard's reagent used (BDH). Fisher's reagent grade was far superior, and gave adequate results. Although treatment with Girard's T reagent resulted in recovery of fairly pure aldehyde ( $\sim 95\%$  purity), yields were quite low, being at the maximum 50%.

An alternative, more productive route to 2,2-dimethyl-1-ace-naphthenecarboxaldehyde was therefore sought. Corey and Chaykovsky (130) have recently reported the chemistry of the nucleophylic ylid, dimethyloxosulfonium methylide  $((\text{CH}_3)_2\text{SOCH}_2)$ , particularly its reaction with certain electrophilic unsaturated linkages such as  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{C}=\text{S}$ , as well as  $\text{C}=\text{C}$ . The reactions apparently involve transfer of a methylene group to the unsaturated linkage, with formation of an oxirane in the case of ketones and aldehydes. The epoxide rings can subsequently be opened using a Lewis acid, as indicated.







removed by chromatography on neutral alumina, but no oxirane could be isolated at all. It was noted that the addition of the reaction mixture to the column of alumina evolved heat, indicating the occurrence of some reaction with the alumina. Indeed, benzene and ether elutions removed all the starting ketone, while final methyl alcohol elution yielded an impure oil, which was shown to be mainly the desired aldehyde (XCIX). Ring opening and rearrangement had thus occurred, although this in itself is not surprising, in view of the fact that alumina can act as a Lewis acid. The  $\text{BF}_3$ -catalyzed rearrangements were not carried out on the reaction mixture of oxirane and starting ketone, since a mixture of initial ketone and the aldehyde would result, and such a mixture could not be separated by column chromatography. Repeated chromatography with benzene as eluant finally yielded quite pure aldehyde, but yields had been curtailed drastically ( $\sim 30\%$ , taking into consideration the amount of recovered ketone).

In all of the reaction steps undertaken to this point starting from 1-naphthaleneacetic acid, the yields had varied from 80-100%, formation of the aldehyde being the only poorly productive step in the overall synthetic scheme. Additional work could perhaps remedy this situation.

The infrared spectrum (Fig. 25) of the aldehyde showed the characteristic aldehyde absorption at  $2725\text{ cm}^{-1}$  (132), as well as the carbonyl band at  $1718\text{ cm}^{-1}$ . The NMR (Fig. 19) showed the aldehyde proton at  $\tau=0.45$  (doublet,  $J=4.0\text{ cps}$ ), and the remaining  $\text{C}_1$ -hydrogen at  $\tau=6.13$



(doublet,  $J=4.0$  cps).

Attempts to prepare the oxirane CI from the reaction between 2,2-dimethyl-1-methyleneacenaphthene (XCV) and perbenzoic acid or m-chloro-perbenzoic acid in chloroform solution were unsuccessful. The NMR spectra of the reaction mixtures indicated the presence of mainly starting material, and possessed none of the characteristic oxirane signals noted earlier.

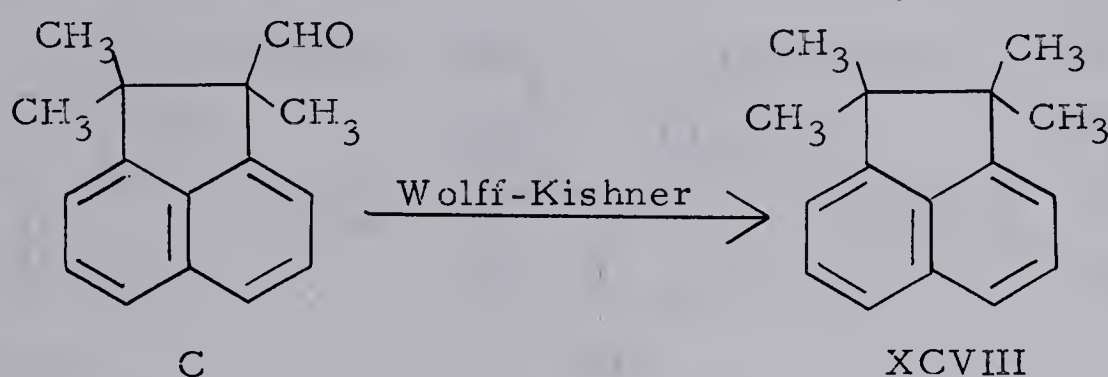
The strongly activating aldehyde group present in the molecule made further alkylation at the  $C_1$ -position of XCIX a relatively easy matter. As in the previous alkylations described in this work, sodium hydride-methyl iodide treatment in benzene furnished the fully substituted aldehyde, 1,2,2-trimethyl-1-acenaphthenecarboxaldehyde (C), isolated as a crystalline solid. The infrared spectrum (Fig. 26) indicated the expected bands at 2725 and 1720  $\text{cm}^{-1}$  for the aldehyde group, while the NMR spectrum (Fig. 20) revealed a singlet at  $\tau=0.84$ , in addition to signals for the aromatic protons and those for three different methyl groups.

Now that the trimethylaldehyde (C) was available for the preparation of tetramethylacenaphthene, a number of possibilities were envisioned, three of which were attempted: 1) Wolff-Kishner reduction of the aldehyde, 2) lithium aluminum hydride reduction of the corresponding p-toluenesulfonylhydrazone, and 3) hydride reduction of the p-toluenesulfonate.

Wolff-Kishner reduction by means of the hydrazone and potassium hydroxide in diethylene glycol yielded an oil which consisted of two components,



shown by GLC to be in a 15:85 ratio. Solidification and recrystallization from alcohol gave a 43% yield of a solid material, melting at 43.5-44.5 °, and considered to be of 98% purity by GLC. Sublimation produced small white crystals, melting at 57-58°. These were shown to be 1,1,2,2-tetramethylacenaphthene (XCVIII) by elemental analysis and NMR spectroscopy.



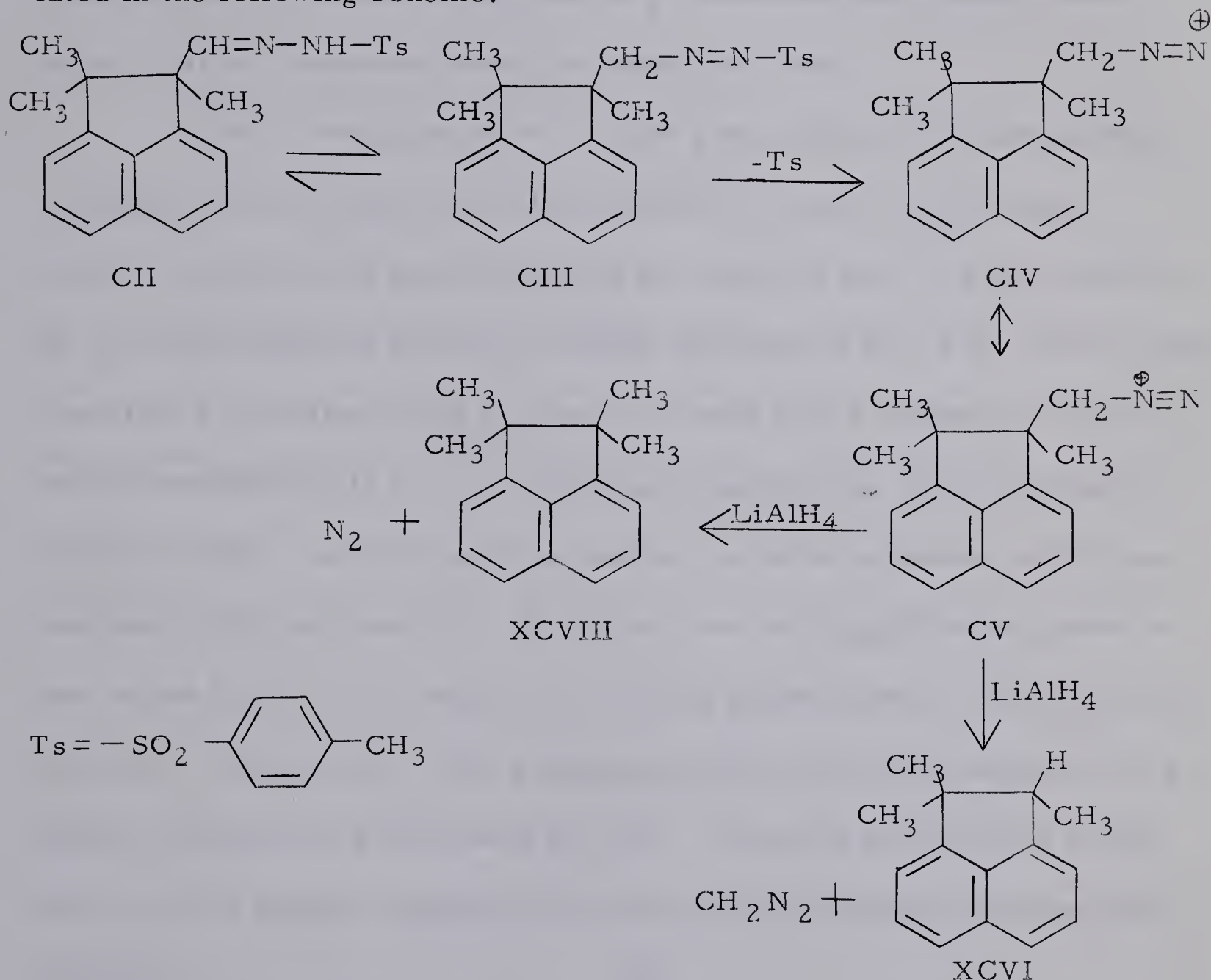
The identity of the 15% impurity was not determined.

Caglioti and Grasselli (133) have observed that the treatment of p-toluenesulfonylhydrazone derivatives of aldehydes and ketones with lithium aluminum hydride or sodium borohydride in methyl alcohol, THF, or dioxan, resulted in the reduction of a carbonyl group to CH<sub>2</sub>. Traces of unsaturated compounds were also formed, but yields of the reduced product were in general quite good, reaching as high as 80%. In the application of this reaction scheme to our work, 1,2,2-trimethyl-1-acenaphthenecarboxaldehyde p-toluenesulfonylhydrazone (CII, NMR spectrum in Fig. 21) was prepared in the usual manner. Reduction by excess lithium aluminum hydride in anhydrous THF resulted in the formation of three products as indicated by GLC, one being rather small (5%), the remaining two being present in approximately equal quantities. By comparison with retention times of authentic samples, these two products were identified as 1,1,2,2-



tetramethylacenaphthene (XCVIII) and 1,1,2-trimethylacenaphthene (XCVI).

The formation of the latter compound, whose presence was also indicated by a quartet and non-identical methyl groups in the NMR spectrum, must have involved a reductive cleavage of a carbon-carbon bond, and is postulated in the following scheme.

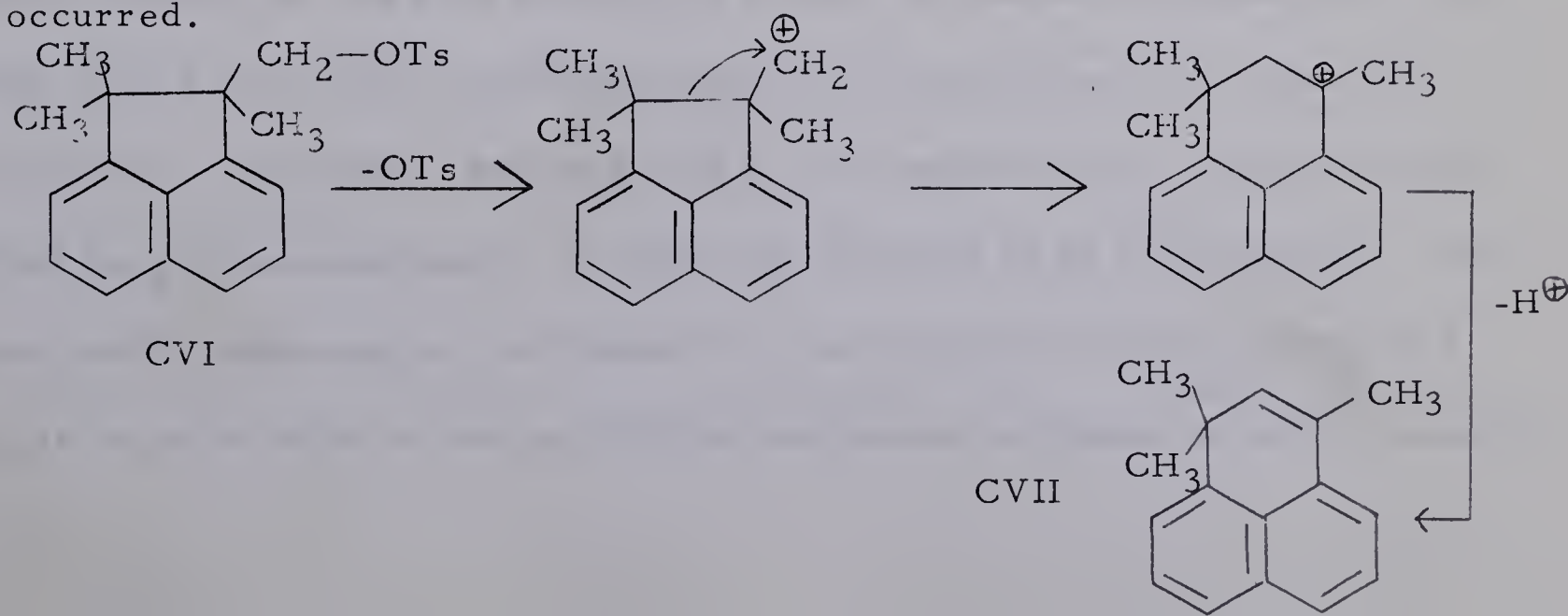


The reduction sequence undoubtedly involves a tautomerization of CII to CIII, which by loss of the p-toluenesulfonyl group can yield the intermediate CIV and hence the resonance form CV. Hydride attack on intermediate CV can now be visualized at two distinct locations; one involving attack at

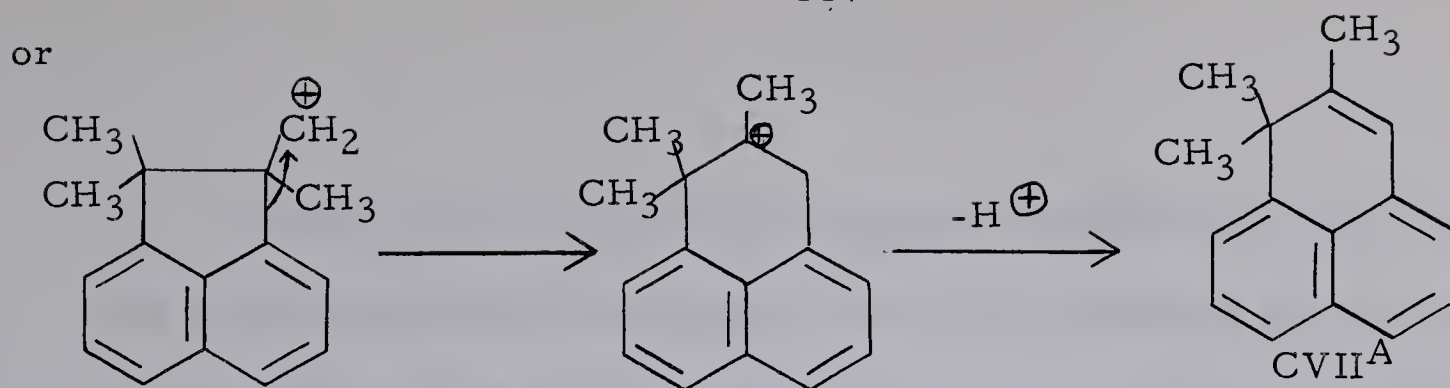


the methylene group resulting in formation of the tetramethyl derivative with the displacement of nitrogen, while the alternate possibility involves attack at C<sub>1</sub>, eliminating a diazomethane moiety, thus yielding 1,1,2-trimethylacenaphthene by carbon-carbon bond fission. The eliminated diazomethane molecule, as well as the p-toluenesulfonyl group, would undergo further reduction under the conditions used.

The third method proposed for the preparation of the tetramethyl compound involved reduction of the aldehyde C to the corresponding primary alcohol (NMR spectrum in Fig. 22), which in turn was converted to the p-toluenesulfonate giving CVI (NMR spectrum in Fig. 23). Even though quantitative reduction of the p-toluenesulfonate of 2,2-dimethyl-1-hydroxymethylacenaphthene to 1,1,2-trimethylacenaphthene by lithium aluminum hydride in ether had been observed earlier, similar reduction of CVI gave completely different results. In fact not one, but five different products were noted by GLC, the main fraction being approximately 75% of the total mixture. Furthermore, only a maximum of 2 to 4% of the expected tetramethyl derivative was detectable by GLC. Isolation and analysis of the main reaction product suggested that either of the following reactions had occurred.





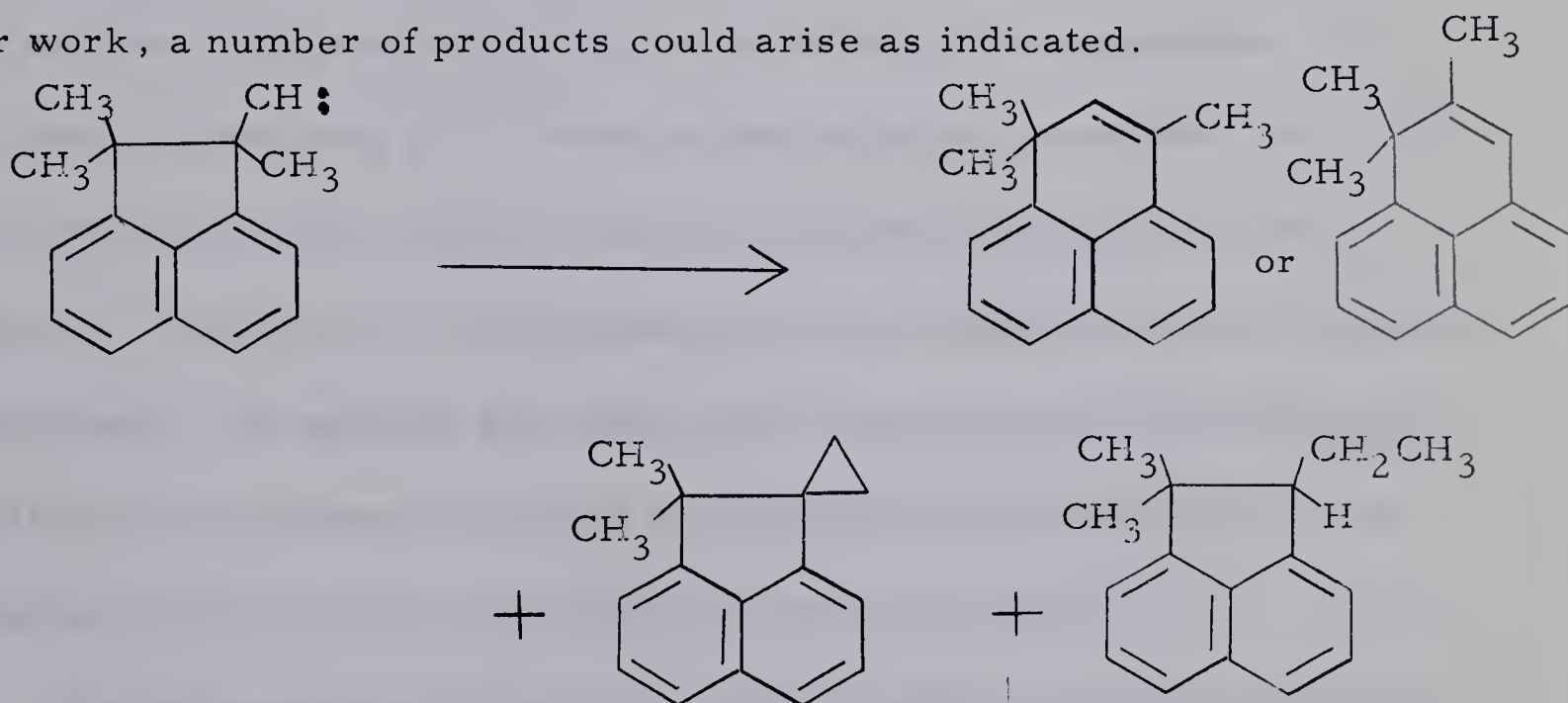


Evidence for the formation of 1,1,3-trimethylphenalene (CVII) or 1,1,2-trimethylphenalene (CVII<sup>A</sup>) is based on spectral data as well as elemental analysis. In the infrared spectrum (Fig. 27), absorption in the double bond region was present at  $1657\text{ cm}^{-1}$ , while the NMR spectrum (Fig. 24) indicated six aromatic protons, one vinyl hydrogen ( $\tau=3.68$ ,  $J \simeq 1\text{ cps}$ ), a fine doublet ( $J \simeq 1\text{ cps}$ ) at  $\tau=8.0$  integrating for three protons, and a sharp singlet at  $\tau=8.55$  integrating for six protons. These data are further supported by a parent peak at  $m/e = 208$  in the mass spectrum, the exact value expected for a compound  $\text{C}_{16}\text{H}_{16}$ . By comparison of the NMR spectrum with that of 2a,3-dihydroacenaphthene (CX, Fig. 28), structure CVII<sup>A</sup> may be favored. In compound CX, the vinyl-proton signal  $\propto$  to the aromatic ring occurs at  $\tau=3.60$ , while that of the  $\beta$ -proton occurs at  $\tau=4.22$ . This suggests that the olefinic proton in the phenalene product is situated  $\propto$  to an aromatic ring as in CVII<sup>A</sup>. In the light of the hydride ions present in the medium, it seems indeed surprising that a Wagner-Meerwein shift as indicated did occur. Generally, it would be expected that intermediate carbonium ions are trapped by hydride species, as has been shown by a number of research groups (134, 135). On the other hand, "free" carbonium ions may not be present if a concerted mechanism is operative. Perhaps such a rearrangement can occur by simply heating the p-toluenesulfonate, or under the influence of an acid catalyst. Additional work concerning the mechanism of rearrangement as well as final and conclusive proof of the structure CVII<sup>A</sup> by independent synthesis would be required.



Both reduction of the p-toluenesulfonylhydrazone and, in particular, the p-toluenesulfonate have shown that introduction of the final methyl substituent into the C<sub>1</sub>-C<sub>2</sub> bridge of acenaphthene cannot always be completed successfully. Steric inhibition, eclipsing of the substituents, internal molecular strain, or a combination of these factors, may perhaps be responsible for the anomalous results obtained in this portion of the work.

Recent work on the base-catalyzed decomposition of p-toluenesulfonylhydrazones at elevated temperatures (136-138) has indicated that a carbenic process is involved, which may undergo further ring expansion, insertion, or a neophyl-type rearrangement. If such a carbene mechanism is possible in our work, a number of products could arise as indicated.



However, failure to isolate or detect any of these products by NMR seems to exclude a carbenic intermediate in the p-toluenesulfonylhydrazone (CII) reduction. Such a process may have occurred during the p-toluenesulfonate (CVI) reduction with subsequent ring expansion to give 1,1,3-trimethyl-



phenalene, although analogous cases have not been encountered elsewhere. Judging from the different products obtained from the p-toluenesulfonylhydrazone (CII) and p-toluenesulfonate (CVI) reductions, it is clear that different reaction mechanisms are operative. The slight difference in experimental conditions lies only in the reflux temperatures of the solvent media used (THF versus ether).

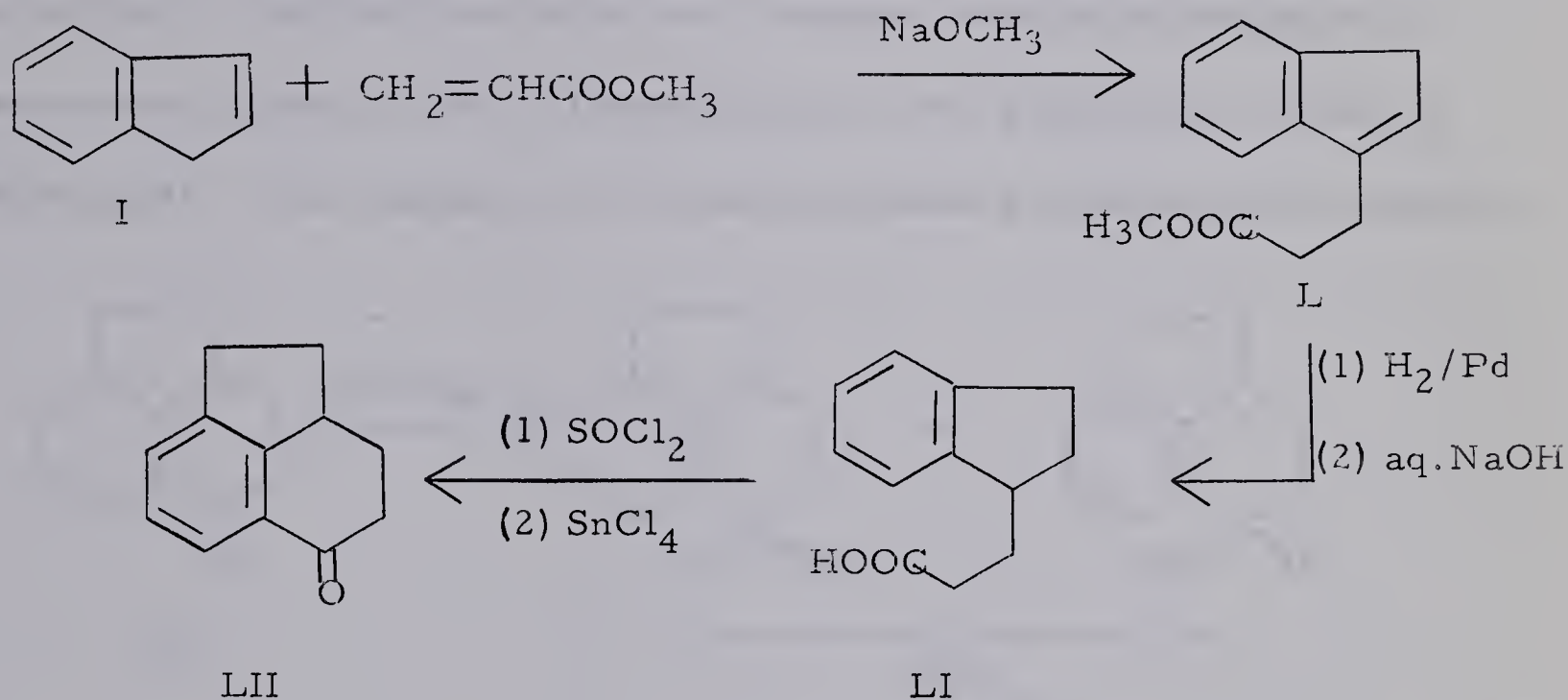
#### G. The Preparation of Hydrogenated Acenaphthene Derivatives

In addition to the C<sub>1</sub> and C<sub>2</sub> methylated species, authentic reduced acenaphthenes were required because of the possibility of Birch reduction of the aromatic ring system during the metalation of acenaphthene. For the purpose of obtaining their chemical and physical properties, 2a,3,4,5-tetrahydroacenaphthene, and two isomeric dihydroacenaphthenes were prepared. The latter two compounds were 2a,5-dihydro- and 2a,3-dihydro-acenaphthene. An attempt was made also to synthesize the third isomer, 4,5-dihydroacenaphthene according to literature directions (139), but in our hands repetition of the experiments were unsuccessful.

For the syntheses of two of the above-named compounds, 2a,3,4,5-tetrahydro-5-acenaphthenone (LII) was required. This was prepared as described in the literature by a sodium methoxide-catalyzed Michael addition of methyl acrylate to indene, to produce methyl  $\beta$ -(3-indenyl)-propionate (L) in 61% yield (140). Following the method of Rapoport and Pasky (141) this indene derivative (L) was reduced to the indanyl ester and



saponified to the corresponding acid (LI). The acid was changed to the acid chloride which in turn was cyclized in benzene, in the presence of anhydrous stannic chloride, by the procedure of Anderson and Wade (55) to LII in 96% yield.

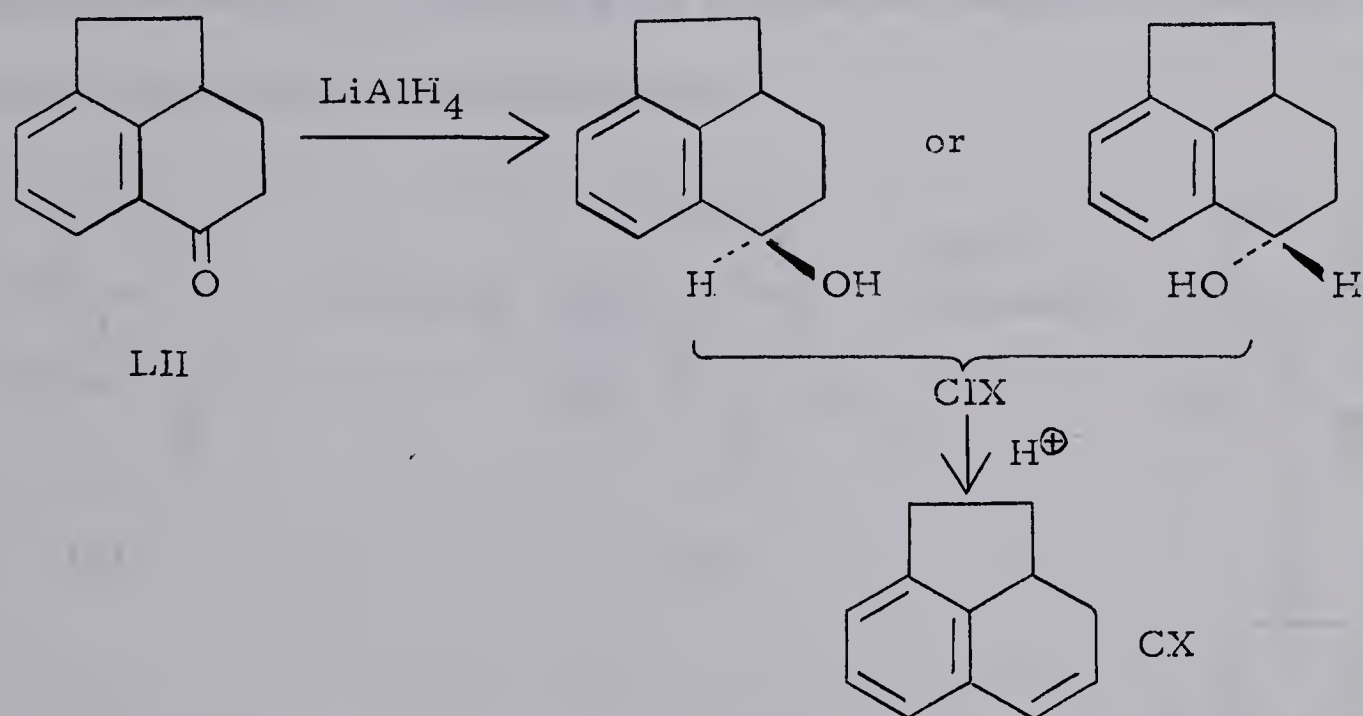


From ketone LII, 2a,3,4,5-tetrahydroacenaphthene (CVIII) was obtained by the familiar Wolff-Kishner reaction. Compound CVIII could also be prepared by following the reduction procedure of Johnson and Glenn (142). These workers hydrogenated acenaphthene in a bomb with the calculated amount of hydrogen at  $110^\circ$  and approximately 1000 p.s.i (95% yield). The ultraviolet spectrum (Fig. 30) of this compound showed strong aromatic absorption at  $\lambda_{\text{max}} = 208 \text{ m}\mu$  ( $\epsilon = 14800$ ), with weak absorptions at  $\lambda_{\text{max}} = 268$  and  $276 \text{ m}\mu$  ( $\epsilon = 600$ ).

Reduction of the ketone (LII) with lithium aluminum hydride in ether was easily accomplished, resulting in a solid product, (CIX), which, after two recrystallizations from aqueous methyl alcohol melted at  $95-96^\circ$ .



Although a hydride reduction of the ketone had not been reported before in the literature, reduction using sodium and alcohol was known (141), but was reported to have given the alcohol as an oil, boiling at 158-160° at 18 mm. Our infrared spectrum of the product CIX indicated that it was an alcohol. The NMR spectrum was consistent with the formulation CIX and showed signals at  $\tau=5.15$  (broad triplet,  $J=7.5$  cps) and 7.53 (sharp OH-singlet). The existence of two distinct isomers as shown in the reaction



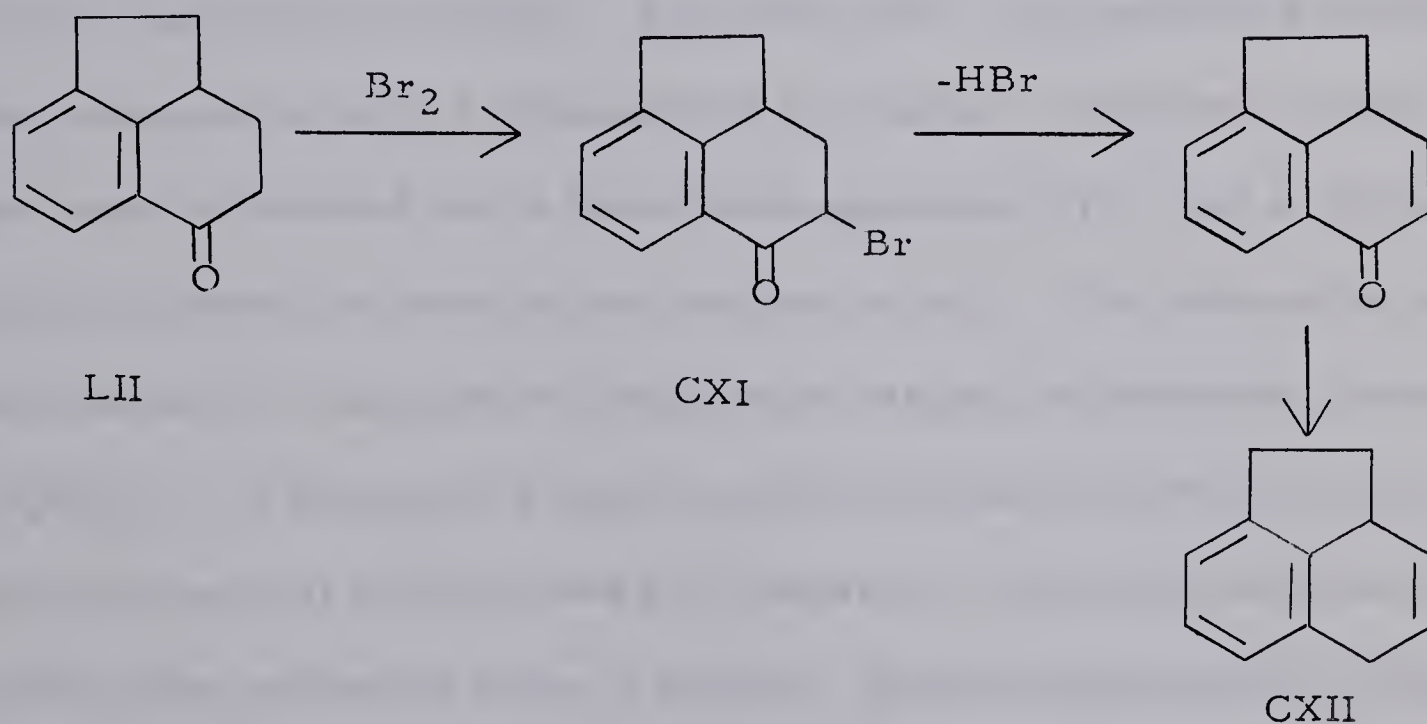
scheme is quite possible, and this may account for the difference in chemical and physical properties observed by us compared to those reported (141).

Heating the alcohol (CIX) with solid oxalic acid yielded the olefin, 2a,3-dihydroacenaphthene (CX), whose NMR spectrum (Fig. 28) showed two vinylic protons at 3.60 and 4.22  $\tau$ . The lower-field signal gave the expected quartet ( $J=9.78$  and 2.93 cps) for the hydrogen  $\alpha$  to the benzene ring, which also indicated additional coupling ( $J=0.60$  cps) with the second allylic proton. The signal at  $\tau=4.22$  was an overlapping seven-



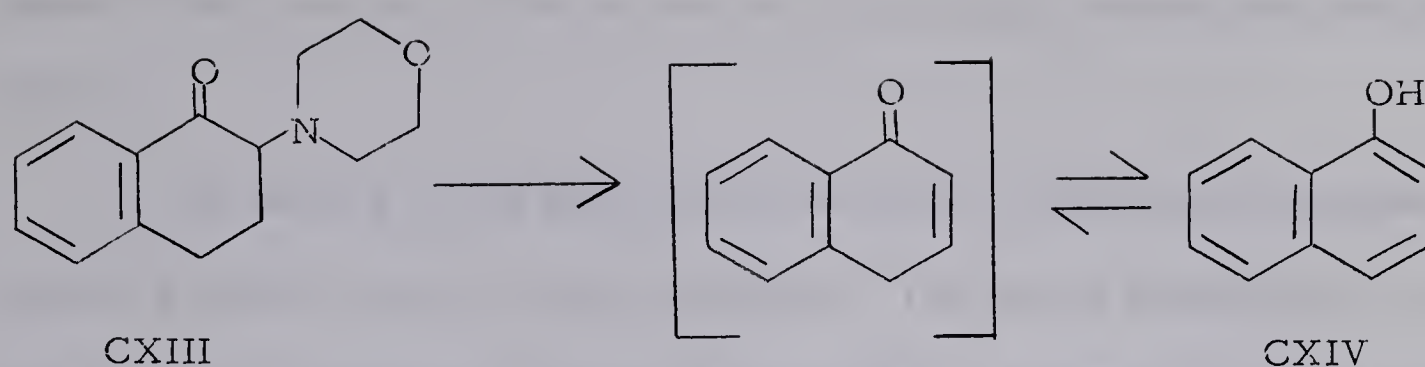
peak multiplet. Double bond absorption in the infrared at  $1623\text{ cm}^{-1}$  came in the expected region. In the ultraviolet spectrum (Fig. 31), a maximum at  $\lambda_{\text{max}} = 266\text{ m}\mu$  ( $\epsilon = 9250$ ) indicated that a conjugated olefinic double bond was present (see Table X, p.126)

One possible route to the non-conjugated isomer 2a,5-dihydro-acenaphthene (CXII) involved bromination of the ketone LII. Dehydrobromination of the resulting product (CXI) should lead to an  $\alpha,\beta$ -unsaturated ketone, from which the desired acenaphthene could be obtained by reduction of the carbonyl function.



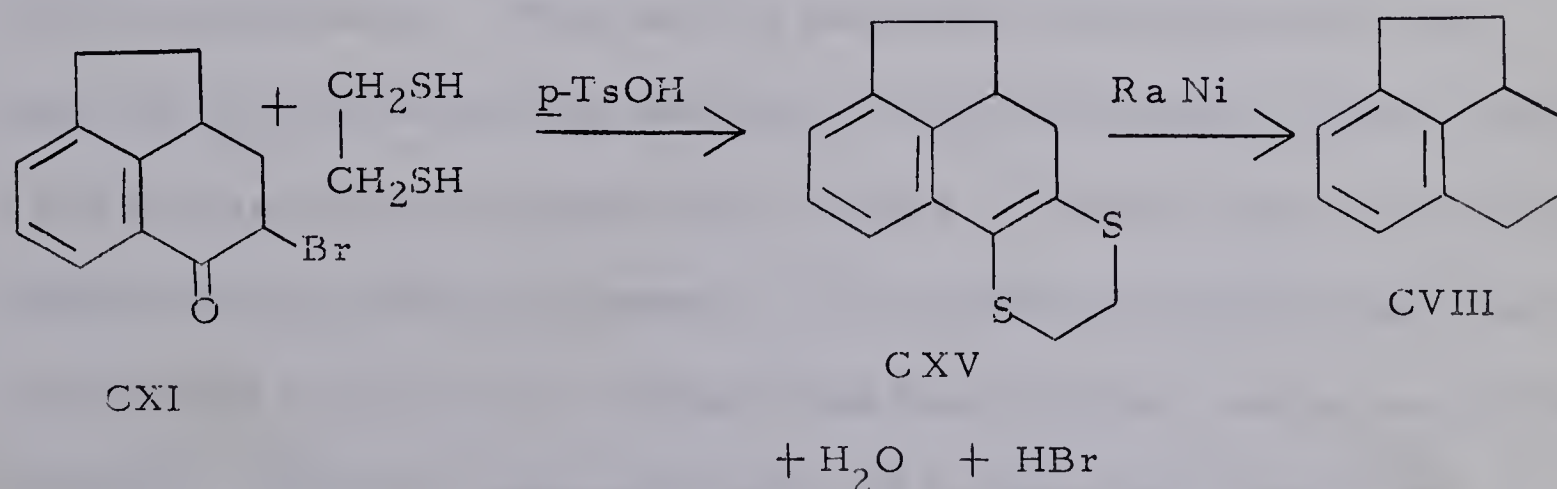
This proposal was discouraged, however, by the report of Dauben and co-workers (143), who found that 2-morpholino-1-tetralone (CXIII) under Willgerodt reaction conditions yielded 1-naphthol (CXIV) as the major product. This compound presumably arose by elimination of the amine to form the  $\alpha,\beta$ -unsaturated ketone, which then was stabilized by aromatization to CXIV.





A similar enolization reaction in our case to yield 5-acenaphthenol would seem very likely, particularly under the either alkaline or acidic conditions required for carbonyl reduction.

Consequently the carbonyl group of compound CXI\* required protection prior to dehydrobromination. To achieve this, acid-catalyzed ketalization was attempted using 1,2-ethanedithiol in toluene. However, not only was water eliminated into a Dean-Stark apparatus (111), but a copious amount of hydrogen bromide was evolved as well. The pale-yellow solid obtained as the final product contained no halogen and analyzed correctly for  $C_{14}H_{14}S_2$ . It possessed a parent peak in the mass spectrum at  $m/e = 246$ . Although spectral evidence was not conclusive, a structure such as CXV seems quite reasonable since in addition, desulfurization with W-2 Raney



\* 4-Bromo-2a,3,4,5-tetrahydro-5-acenaphthenone (CXI) is a lachrymator and possesses skin-irritating properties.



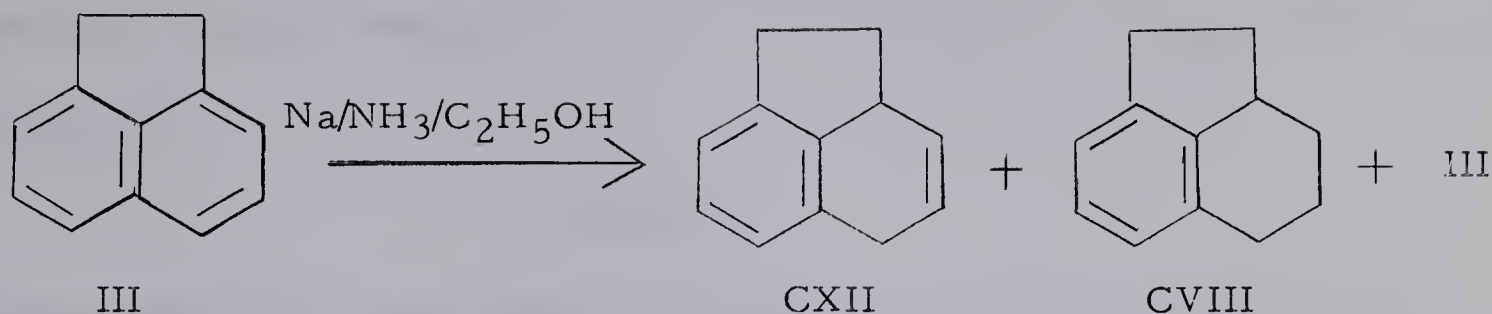
nickel (144) resulted in the formation of 2a,3,4,5-tetrahydroacenaphthene (CVIII).

The failure of the above route to the 2a,5-dihydroacenaphthene required another path to this compound. The Birch reduction of naphthalene in liquid ammonia is known to proceed in a stepwise fashion (145), 1,4-dihydronaphthalene being the first product formed when two equivalents of sodium are used. Further reduction to 1,4,5,8-tetrahydronaphthalene occurs however, when excess sodium metal is employed. By applying similar conditions to acenaphthene, the 2a,5-dihydro derivative (CXII) should be obtainable. Lebeau and Picon (146) have reported the isolation of 2a,3,4,5-tetrahydroacenaphthene from the sodium-ammonia reduction; however, experimental details were not available.

In our work, addition of two gram-equivalents of sodium metal to acenaphthene in liquid ammonia, in the presence of ethyl alcohol (145), yielded a mixture of three products as shown by GLC. By retention times, the presence of 9% of 2a,3,4,5-tetrahydroacenaphthene and 18% of starting material was indicated. The remaining 73% was believed to be due to a dihydroacenaphthene. When half the calculated amount of sodium was used, the ratio of tetrahydro: dihydro: acenaphthene became 6:68:26, while a 20% excess of metal changed this to 12:84:4. The last traces of starting hydrocarbon are difficult to remove. The reaction conditions finally used involved 33% excess metal, although even then a few per cent of acenaphthene remained. However, this could nearly all be removed by fractional



distillation.



Bromination of the reaction mixture to facilitate separation of the olefin from CVIII and III afforded a dibromide, which could be debrominated successfully with magnesium to a colorless oil which turned yellow on standing at room temperature. The infrared spectrum of CXII indicated unsaturation ( $1635\text{ cm}^{-1}$ ), while in the NMR spectrum (Fig. 29) a vinyl proton signal at  $4.16\tau$  integrated for two protons. The vinyl protons showed surprisingly little coupling which could only be resolved by a high-resolution spectrometer. Analysis on an HR-100 instrument showed, in addition to two small peaks 23.48 cps. apart, six other signals with coupling values varying between 1.20 and 1.72 cps. Elemental analysis agreed with the proposed structure, as did the mass spectrum, which exhibited a parent peak at  $m/e = 156$ . As would be expected, the ultraviolet spectrum (Fig. 32) was nearly identical to that of 2a,3,4,5-tetrahydroacenaphthene, with absorptions at  $\lambda_{\text{max}} = 266$  and  $273\text{ m}\mu$  ( $\epsilon = 500$ ).

Comparison of the ultraviolet spectra of all three reduced acenaphthenes with those in the naphthalene series (147) indicates a nearly identical relationship, with all values being virtually the same (see Table X). Birch reduction of the two molecules also follows a close parallel, with the



exception that in the acenaphthene case one ring is completely reduced to give a tetrahydro compound, while in naphthalene both rings undergo partial reduction.

TABLE X

Comparison of UV absorptions of reduced acenaphthenes with reduced naphthalenes and styrene derivatives (in ethyl alcohol)

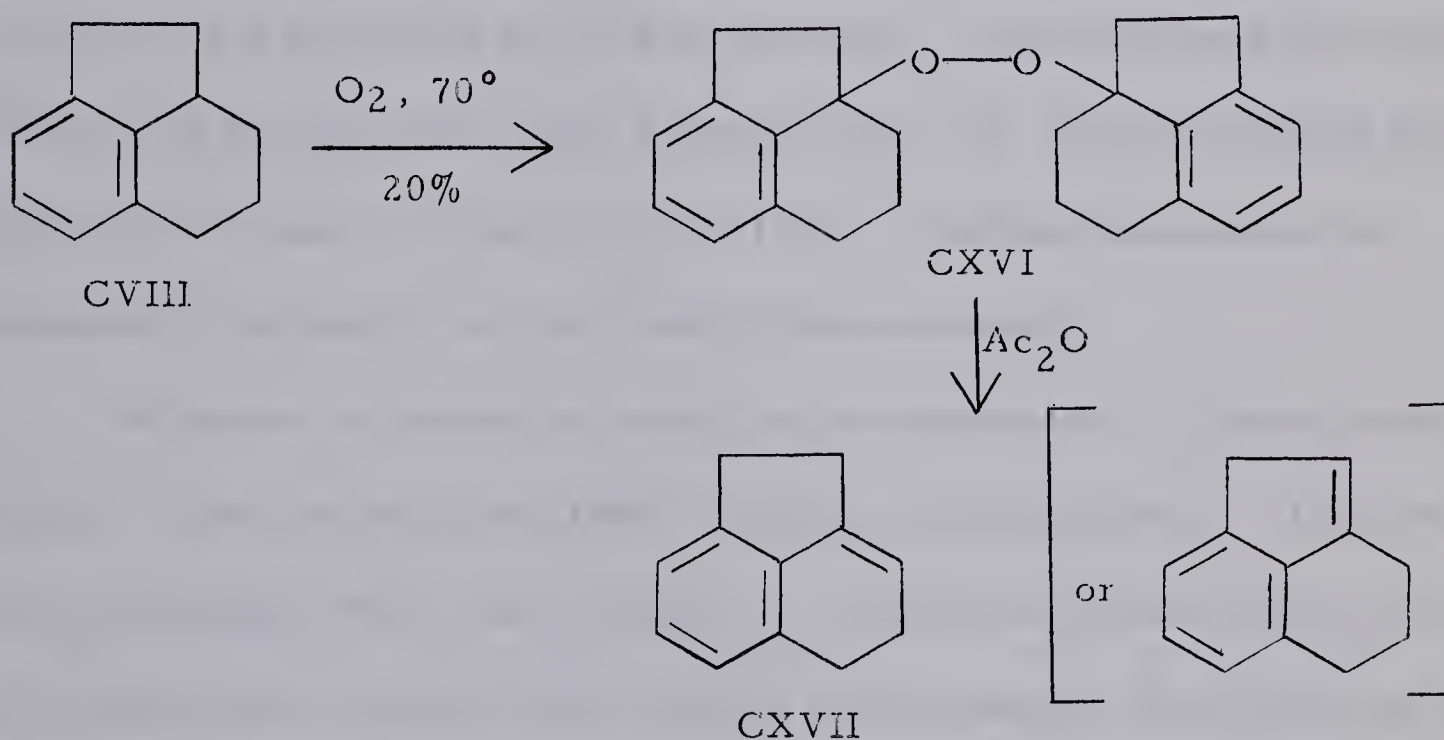
Compound	$\lambda_{\max}$ m $\mu$	$\epsilon$	Reference
1,2,3,4-tetrahydronaphthalene	260	380	147
	266.5	559	
	273.5	605	
1,2-dihydronaphthalene	259	9449	
	296	180	
1,4-dihydronaphthalene	262	332.5	
	267	439	
	274	449	
2a,3,4,5-tetrahydroacenaphthene	268	600	148
	276	600	
2a,3-dihydroacenaphthene	266	9250	
	302	540	
2a,5-dihydroacenaphthene	266	500	
	273	500	
styrene	244	12000	
	282	450	
$\beta$ -methylstyrene	245	12600	
	280	660	
	289	400	

Although both 2a,3- and 2a,5-dihydroacenaphthene were shown to be stable under the thermal GLC conditions (200°), the 2a,5- compound



was rearranged under alkaline conditions to the more stable 2a,3-derivative, where the double bond is conjugated with the aromatic ring system. Reflux with potassium tert-butoxide in tert-butyl alcohol accomplished this transformation, but acidic conditions did not bring about any rearrangement whatsoever.

An attempt to synthesize the third isomer, 4,5-dihydroacenaphthene (CXVII) by a route reported in the literature was unsuccessful in our hands. Although Treibs and Thörmer (139) have reported its preparation in low yield according to the indicated scheme below, we were unable to



reproduce their results, failing to obtain any of the intermediate peroxide (CXVI).

#### H. The Metalation of Acenaphthene

Before embarking upon a study of the methylation of metalated acenaphthene, wherein a preliminary experiment had shown the presence of at least eight products, it was deemed necessary to investigate first



the metalation reaction itself. Much useful information might become available in addition to that concerning the evolution of hydrogen gas. The results of these experiments are shown in Table XI.

Volumes of gas (205-210 ml) identical to those found in the indene case, were produced when only solvent and metal were refluxed. These contained only traces of hydrogen gas as indicated by mass spectrometry. One notable exception occurred however. When potassium metal was heated in refluxing DME for nearly 24 hours, the volume of gas increased to 315 ml, but contained only 3% of hydrogen. Both methane and ethylene, 17% and 2% respectively, were found in this case, thus accounting for the observed increase in volume above 210 ml. Solvent decomposition, postulated previously, is thus clearly demonstrated.

Mixtures of potassium metal and acenaphthene (1:1 mole ratio) reacted rapidly in refluxing DME, yielding a black solution. Consumption of the potassium metal was complete. Varying the reflux times from 2 to 8.5 hours in three experiments caused little change in the volume of gas collected, this being 235 to 250 ml, containing hydrogen to the extent of 4 to 8%. Although the one gram-equivalent of lithium metal was not all consumed during the metalation, similar quantities of gas (255-260 ml) were trapped. These also contained only small amounts of hydrogen. In one instance (expt. 12) where mass spectrometry indicated 9% of hydrogen, methane (3%) and ethylene (7%) were also found.

Unlike indene, and also fluorene, acenaphthene therefore yields very



TABLE XI

Production of hydrogen during the reaction of acenaphthene with lithium or potassium metal in refluxing 1,2-dimethoxyethane (DME)

(0.05 mole of hydrocarbon in 100 ml of DME)

Expt. no.	Metal used	Gram-equivalents of metal used	Amount of metal consumed %	Time of reflux hrs.	Volume of gas collected, ml	Amount of H <sub>2</sub> in collected gas, %	Amount of CH <sub>4</sub> and C <sub>2</sub> H <sub>4</sub> in collected gas, %
1	K	—	—	2	210	<1	—
2	K	—	—	23.5	315	3	CH <sub>4</sub> 17 C <sub>2</sub> H <sub>4</sub> 2
3	K	1	100	2	235	~4	—
4	K	1	100	3.5	250	7-8	—
5	K	1	100	8.5	245	5	—
6	K	2	81	4	575	~40	—
7	K	2	92	22	775	53	traces
8	K	2	nearly all	22.5	890	~60	—
9	K	2	84	22.5	625	48	—
10	Li	—	—	22	205	—	—
11	Li	1	80	22.5	255	<1	—
12	Li	1	nearly all	22.5	260	9	CH <sub>4</sub> 3 C <sub>2</sub> H <sub>4</sub> 7
13	Li	2	~90	22.5	350	13	CH <sub>4</sub> 6 C <sub>2</sub> H <sub>4</sub> 9
14	Li	2	83	22.5	340	13	CH <sub>4</sub> 7 C <sub>2</sub> H <sub>4</sub> 10



little hydrogen gas when it reacts with an equivalent amount of potassium or lithium metal in the ether solvent DME. If all the hydrogen is in fact derived from a reaction such as equation (e) (p. 57) with indene, it would account for just  $\sim 5\%$  of reaction. Considering the "acidity" of acenaphthene and also its likeness to the naphthalene molecule, this observation is not surprising. Naphthalene is known to react readily with alkali metals in ethereal solvents, "the reaction consisting of the transfer of an electron from the metal into the lowest vacant orbital of the naphthalene molecule, and the transfer of the resulting metal ion into solution, where its energy drops due to solvation." (71). Acenaphthene thus may be expected to undergo the same reaction, in fact it may do so even more readily if comparison to its dehydro derivative, acenaphthylene, is valid. Hoijsink and co-workers (150) have tabulated the reduction potentials of aromatic hydrocarbons ( $E_1$ ), and of their univalent anions ( $E_2$ ), against sodium-biphenyl in DME, and found that the values for acenaphthylene were greater than those of a number of hydrocarbons, including phenanthrene, anthracene, benzopyrenes etc.. The  $E_1$  and  $E_2$  values reported for acenaphthylene were 1.12 and 0.56 volts respectively, while  $E_1$  for naphthalene was 0.09 volts. No  $E_2$  value was available due to the instability of the naphthalene dianion, although preparation of the dianion has been reported quite recently (151). Whether acenaphthene is closer to naphthalene or acenaphthylene in the electrochemical series cannot be decided. Nevertheless, a definite electron affinity of acenaphthene can be inferred by comparison with the above two compounds.



The use of two gram-equivalents of lithium metal raised the volume of collected gas to 350 ml, and increased the amount of hydrogen gas to 13%. In contrast, the addition of a second equivalent of potassium brought about far greater changes. Large increases in gas evolution were noted, with total volumes now ranging from 575 ml to 890 ml, depending upon the amount of metal consumed. Addition of a second molar equivalent of potassium metal therefore caused a volume increase of approximately 335-650 ml. This increase was made up largely of hydrogen gas as shown by mass spectrometric analysis. In fact, the largest increase (650 ml) corresponds almost to the volume expected when 0.05 mole of acidic hydrocarbon reacts completely with 0.05 mole of metal to give hydrogen and a salt.

Although the exact position from which a proton is removed has not been determined, it seems rather unlikely that a  $C_1$ - or  $C_2$ -hydrogen is involved. Since virtually no hydrogen abstraction from these positions occurred when one equivalent of metal was used, there seems to be no plausible reason why such a reaction should take place when two equivalents of metal are employed. Instead, proton removal from a reduced species present in the reaction mixture seems more likely, resulting in the formation of another anion, or even a dinegatively charged species. This view finds support from later methylation experiments, which indicated increased yields of a number of products, but showed no large increase in 1-methyl-acenaphthene formation.



When the mixture obtained from the reaction of potassium and acenaphthene was treated with dilute aqueous acid, a rapid decolorization from black to orange to yellow took place (cf. naphthalene system (152)). Analysis by GLC on three different columns clearly resolved three products in the ratio of 11:5:84 when one equivalent of potassium was used, and the same products in the ratio of 13:6:81 when two equivalents were utilized (averaged from three experiments each). These figures indicate that very little difference in the final products exists, whether use is made of one or two equivalents of potassium. (This is not so when methyl iodide is added to the metalated material).

By comparative retention times and the NMR spectrum (Fig. 33) of the reaction mixture, the main fraction was found to be the starting material (sharp singlet,  $\tau=6.91$ ). The product obtained in smallest yield (5-6%) could not be identified. Its retention time did not correspond to any of the authentic samples on hand, including 1,8-dimethylnaphthalene. Evidence for this latter compound was never found in any of the metalation runs studied in this work. 1-Ethynaphthalene was not considered as one of the products on the basis of the work reported by Cram and Dalton (68) (see p. 28). In addition to an aromatic signal at 3.1  $\tau$ , the unidentified component exhibited broad, unresolved peaks between 7 and 9.3  $\tau$ , indicating reduction of the acenaphthene molecule.

Some vagueness is associated with the identification of the first peak (11-13%) when one molar equivalent of potassium was used. In the

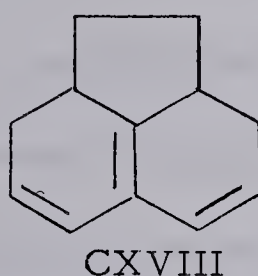


case of the reaction with two equivalents, it was definitely established as 2a,3,4,5-tetrahydroacenaphthene. In the first case where one equivalent of metal was employed, the inability to obtain reproducible results was particularly disconcerting. In two out of four experiments, the NMR spectra (Fig. 33) of the reaction mixtures showed the presence of olefinic protons at  $\tau=3.55$  and 4.2, while in the remaining two experiments none could be found whatsoever (Fig. 34). Nevertheless, the GLC patterns of the reaction mixtures were identical in all cases, with the retention time of the first component being equal to that of 2a,3,4,5-tetrahydroacenaphthene.

The observed vinylic protons (Fig. 33), which by integration of the peaks seemed to be present to a considerable extent, showed an AB pattern, similar to that of 2a,3-dihydroacenaphthene (Fig. 28). Instead of two doublets, however, two sets of triplets centered about  $\tau=3.55$  ( $J=10$  and 2 cps) appeared, while the second proton at 4.2  $\tau$  appeared as a multiplet. In addition, two broader signals at 6.55 and 6.74  $\tau$  were noticeable. In the infrared, the unsaturation was indicated by absorption at  $1640\text{ cm}^{-1}$ . Attempts to isolate this olefinic product met with no success. Both GLC isolation and column chromatography on neutral alumina with Skellysolve B resulted in a product which had lost all its olefinic character, and which was shown to be 2a,3,4,5-tetrahydroacenaphthene by NMR. Additional attempts to obtain this unknown compound by further metalations, which would permit a closer study as to its structure,



failed, as was mentioned earlier. The similarity of the olefinic pattern observed in the NMR spectrum to that of 2a,3-dihydroacenaphthene seems to indicate the presence of a conjugated system, which may be able to undergo a further rearrangement. The possibility exists that the unknown compound may possess a structure such as CXVIII. Such a structure



could rearrange to 2a,3,4,5-tetrahydroacenaphthene, the compound obtained after chromatography. Models have indicated that a compound of the above type is structurally quite feasible.

From Table XI the observation can be made that in none of the metalations were two complete equivalents of metal consumed. Although in one case (expt. 8) nearly all the metal had reacted, in general 1.6 to 1.8 equivalents of metal were required. The fact that less than one equivalent of lithium metal was consumed in some cases (expt. 11,12) must be due to the formation of the organometallic derivative on the surface of the metal, thereby excluding further reaction.

Cram and Dalton (68) have also metalated acenaphthene with potassium in DME, but at room temperature for 17 hours. They reported the consumption of 2.1 moles of metal per mole of hydrocarbon, with concurrent formation of two products as analyzed on a silicone gum column. Of the two components, formed in approximately equal yield, one was found



to be starting material, while the second was shown by infrared analysis to be neither 1-ethylnaphthalene nor tetrahydroacenaphthene. Upon repeating their work, following their conditions exactly with the exception that five-fold quantities were taken, we found that indeed 2.1 equivalents of metal were consumed. However four, rather than two products were shown to be present by GLC analysis on three different columns. Chromatography on silicone rubber revealed only two peaks, along with a small shoulder of a third component. From comparative retention times on three columns and the NMR spectrum (Fig. 35) of the mixture, the following product distribution was found: 11% of 2a,3,4,5-tetrahydroacenaphthene, 21% of 2a,3-dihydroacenaphthene, 56% of starting material, and 12% of an unknown compound. Under these mild experimental conditions, it is surprising that more metal was consumed than when refluxing conditions were maintained. The lower temperatures also permitted the identification of the 2a,3-dihydroacenaphthene, which could arise from either direct 1,2-addition, or from 1,4-addition with subsequent rearrangement. Further reduction of this conjugated olefin to the tetrahydro derivative of course could occur quite readily.

The use of lithium metal resulted in the formation of five components, two of which had longer GLC retention times than the products obtained from the acenaphthene-potassium reaction. Area ratios obtained with one equivalent of lithium metal were 1:3:89:3:4, while reaction with two gram-equivalents of metal gave area ratios of 2:3:78:8:9. These figures were the



average obtained from the results of two experiments in each case. Of these five components, only the main fraction, acenaphthene, could be identified. As well, the presence of 2a,3,4,5-tetrahydroacenaphthene could be ruled out on the basis of retention time. The first peak (1-2%) might have been due to a compound with olefinic character, although its concentration in the reaction mixture was too small for reliable identification by NMR (Fig. 36). Signals above  $\tau=7$  in the NMR were characteristic of the unknown constituents.

Due to the presence of too many unidentifiable components, a material balance using an internal standard could not be relied upon to give meaningful results. However, good approximation could be made by weighing the reaction mixture, free from any solvents, then subjecting it to chromatography on neutral alumina. Starting with 7.71 g. (0.05 mole) of acenaphthene, an average weight of 7.8 - 7.85 gm of products was obtained in all cases, regardless of the amounts of potassium or lithium metal introduced. Chromatography of an acenaphthene-potassium reaction mixture on neutral alumina with Skellysolve B yielded 6.05 - 6.10 gm (79% based on initial starting material) of product exhibiting the same peaks on GLC as before. Ether elution removed a further 1.05-1.22 gm (14-16%) of a yellow viscous oil, which did not come off a GLC column at 200°. Final elution with methyl alcohol gave 0.16 gm (2%) of an oily solid which, like the ether fraction most probably consisted of di- or polymeric material. Similar treatment of an acenaphthene-lithium reaction mixture yielded the



three fractions in 70, 16, and 12% yields. In all cases therefore, better than 90 or 95% of the weight of material could be accounted for.

#### I. Methylation of Metalated Acenaphthene

Methylation of the green-black reaction mixtures, obtained by refluxing acenaphthene with potassium metal in DME, with a large excess of methyl iodide was found to be quite complex and generally gave inconclusive and unsatisfactory results. The reaction involving lithium appeared to be relatively quite simple, though here also the results were far from satisfactory.

From the acenaphthene-potassium mixture (1:1 mole ratio), GLC analysis on a column of 25% silicone rubber on Gas-Chrom P revealed five products (15:14:48(25:23):23 mole percent)\*. On Apiezon L the same mixture gave eight components (5:20(12:8):3:8:45:6:13), while on neopentylglycol succinate (NPGS) eleven different constituents were distinguishable (13:8:3(1:2):9(2:4:3):41:10:6:10). This complicated mixture was extremely difficult to analyze. Moreover, the NMR spectrum (Fig. 37) of this mixture was complicated and difficult to interpret. Consequently it was necessary to rely heavily upon comparison of GLC retention times with those of authentic samples, a procedure which is not entirely satisfactory. To make matters worse, very few of the authentic samples could be matched

---

\* The use of brackets after a number, i.e. after a peak, indicates that this peak is poorly resolved into the number of components shown within the brackets. e.g. The 48%-peak is poorly resolved into two products, 25% and 23% respectively.



by retention times with those of the products obtained from the above methylation. In addition, none of the products could be obtained in a pure state by GLC isolation; only fractions of the total reaction mixture could be obtained in which some peaks were more concentrated while others were greatly diminished or were completely absent. By use of these GLC-isolated fractions of the overall reaction mixture, comparative retention times, and NMR spectra the following conclusions could be made:

1. The presence of 2a,3,4,5-tetrahydroacenaphthene to the extent of approximately 10-14% is strongly indicated by retention times on three different columns, although not conclusively proven.
2. By retention time on an NPGS column, no more than 1% or 2% of dihydroacenaphthenes could be present in the reaction mixture.
3. Both the starting material and 1-methylacenaphthene were definitely present in the reaction mixture. From comparative retention times on all three columns, but particularly silicone rubber, the biggest peak (41-48%) was made up largely of these two products, and the relative percentages of each of the two compounds is therefore estimated to be approximately 20-25. This is supported by the strong signals observed in the NMR spectrum (Fig. 37). The characteristic singlet for acenaphthene occurred at  $\tau=6.86$ , while the multiplets between  $\tau=6.3-7.4$  corresponded to those observed for authentic 1-methylacenaphthene.
4. Of the dimethylated acenaphthenes, certainly no more than 3%, if any



at all, of the 1,1-disubstituted derivative could be detected, while the formation of cis-1,2-dimethylacenaphthene could be excluded altogether. Both these determinations were made on the basis of the observed retention times on an NPGS column. The presence of trans-1,2-dimethylacenaphthene of course cannot be eliminated, due to the lack of an authentic specimen.

5. Even though the retention time of a 10% peak on an NPGS column matched that of 1,1,2-trimethyl- and 1,1,2,2-tetramethylacenaphthene, the formation of these two compounds appeared extremely unlikely in view of the very small amount (if in fact any) of disubstitution observed above. On this basis the tri- and tetramethyl derivatives were excluded as possible reaction products.

In addition to the above observations, the NMR spectra also indicated the presence of some olefinic product possessing signals at  $\tau \simeq 3.6$  and  $4.1$ . These signals were present even after column chromatography on neutral alumina, which could indicate that the presence of methyl substituents may prevent rearrangement of the molecule. Furthermore, numerous signals believed to be due to methyl groups, appeared at tau values above  $7.5$ . Small singlets at  $7.5$  and  $7.75 \tau$ , and a doublet at  $7.97 \tau$  ( $J=1.5$  cps) appear to indicate linkage to an electron-withdrawing group, while very strong signals at  $8.67$ - $8.83 \tau$  are apparently positioned at a saturated carbon centre. A two-line signal (possibly a doublet) with a 7 cps separation was also present at very high field,  $\tau=9.58$ .



The use of two equivalents of potassium metal, with 1.76 equivalents having been consumed after 17 hours in refluxing DME, led to surprisingly few differences in results. Notable changes were the appearance or disappearance of a few minor products as seen by GLC analysis; the general percentage-wise increase of most products (also observed by GLC), and the almost complete absence of the starting material as indicated by the NMR spectrum (Fig. 38). Important also is the fact that the amount of 1-methylacenaphthene showed no significant increase, being approximately 20-23% of the total mixture as shown by retention time on an NPGS column. The signals of the  $C_1$ - and  $C_2$ - protons of 1-methylacenaphthene are clearly distinguishable between  $\tau=6.4$  and 7.4; the methyl-doublet is buried beneath the strong signals at  $\tau=8.75$ -8.82. It appears therefore that metalation at  $C_1$  is not favored, even with the introduction of a second equivalent of potassium metal. Analyses by GLC were as follows: silicone rubber - 17:18:32:31:2; Apiezon L - 6:23(13:10):2:14:26:10:16:3; NPGS - 16:11:3:10(6:4):23:16:7:14. As can be seen, a small 2% and 3% peak appeared at the end when silicone rubber and Apiezon columns were used respectively, while two small constituents (1% and 2%) had disappeared from the NPGS analysis. Otherwise all other observations, including spectral, were as before.

In contrast to the great complexity encountered when potassium metal was used, reactions with lithium were much simpler although also unsatisfactory. In fact very little difference existed between the results



of these methylation reactions and those of the metalation experiments described earlier. That is, very little, if any methylation occurred, since the final reaction mixture was composed almost exclusively of starting material, as shown by GLC and the NMR spectrum (Fig. 39). Addition of excess methyl iodide to the metalated hydrocarbon produced very little reaction, with little or no lithium iodide precipitating from solution. However, upon decomposition of the reaction mixture with dilute acid, a vigorous reaction ensued indicating the presence of some reactive species. Even after the reaction mixture was warmed for two hours and more methyl iodide was added, methyl groups were not introduced in substantial amounts. When one equivalent of lithium was used (90-93% was consumed after 17 hours of reflux), 90% of acenaphthene was recovered as shown by GLC, the remaining 10% being distributed among at least five components, the largest of which was 5 to 6% of the total product. The introduction of two equivalents of lithium metal, 65% of which was consumed in 15 hours, lowered the quantity of starting material to 75%, and gave six other constituents sharing the remaining 25% of product in the ratios 2:3:2:5:5:8. The NMR spectrum (Fig. 40) in this case showed some weak signals at about  $\tau=8.65$ , no doubt due to some methyl groups. Even though lithium compounds are known to possess more covalent character and less reactivity (71), these methylation results were nevertheless unexpected.

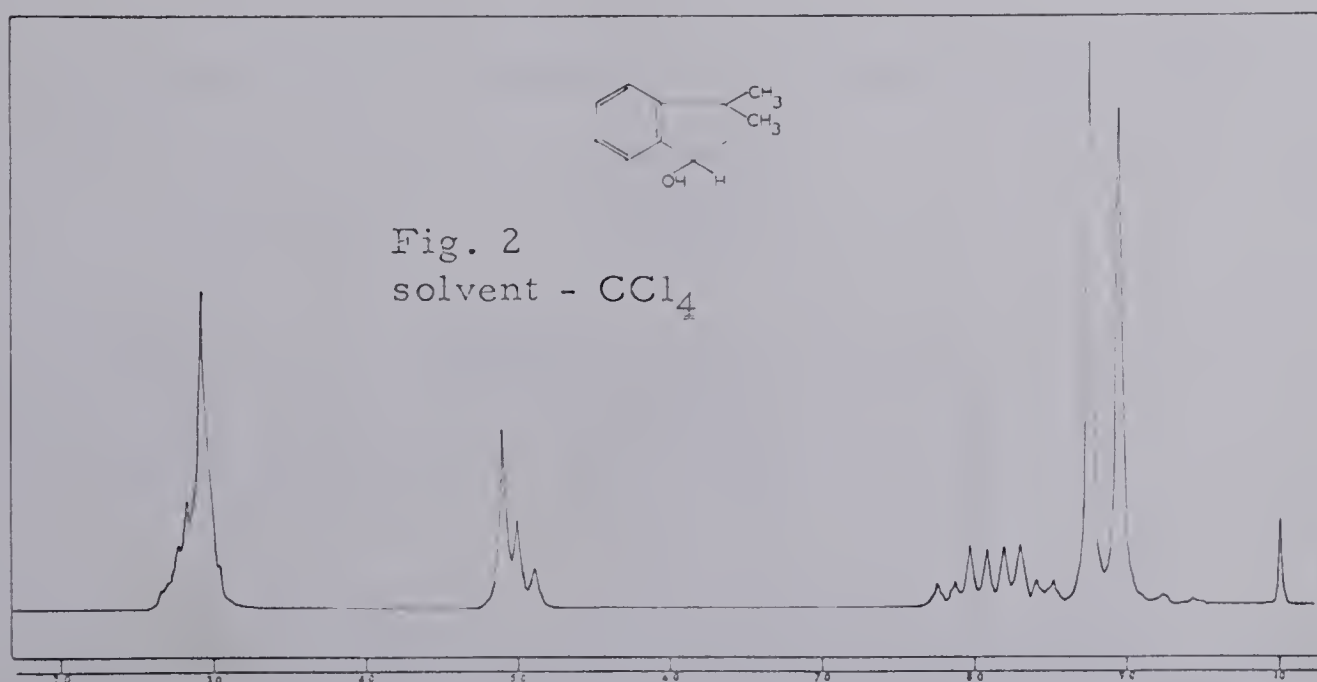
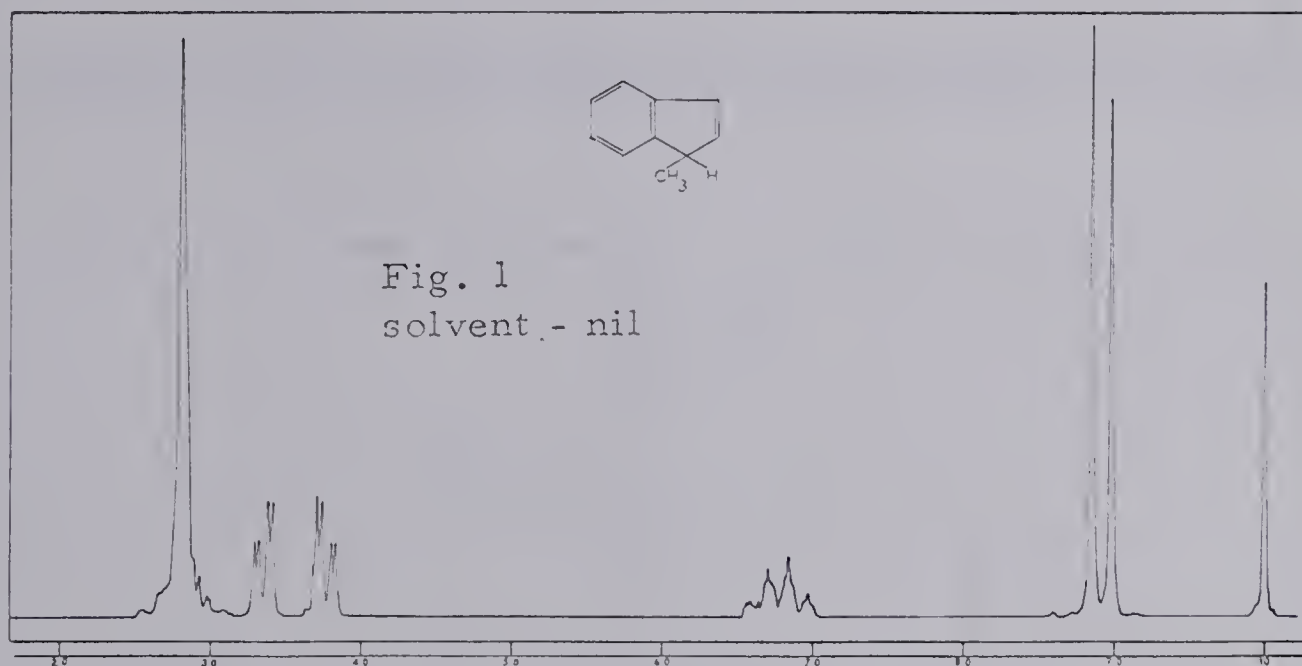
As before, column chromatography on neutral alumina allowed the separation of the analyzable hydrocarbons from any polymeric products



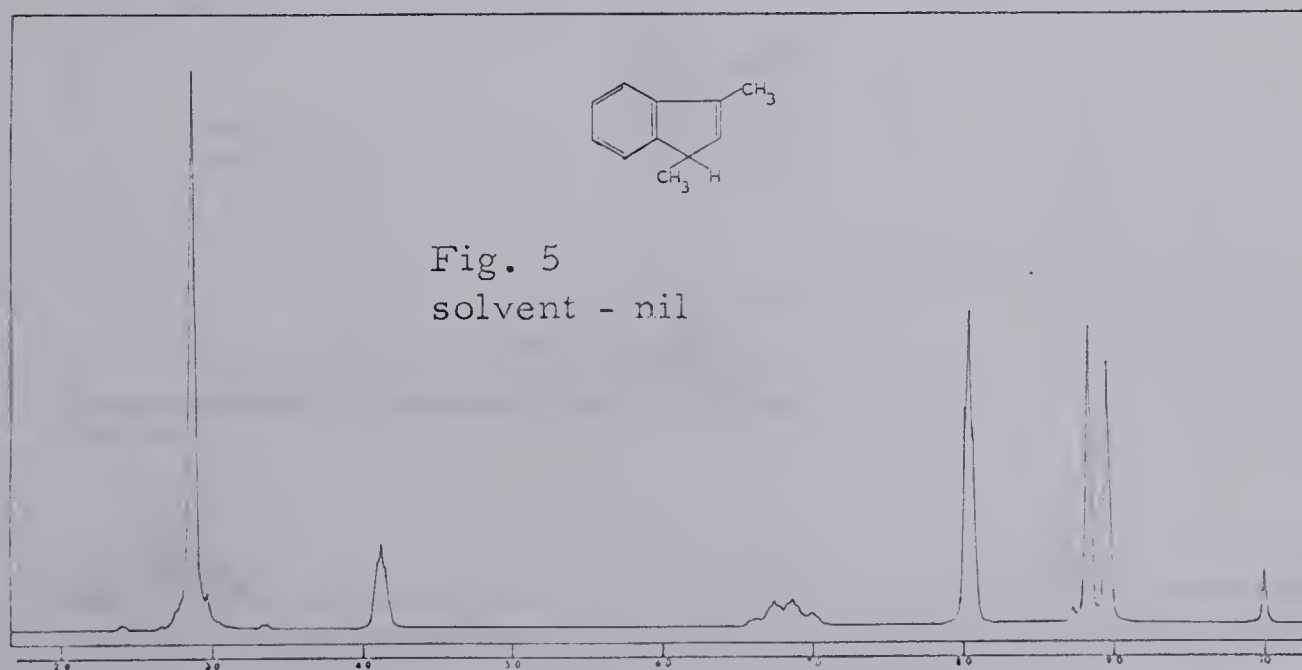
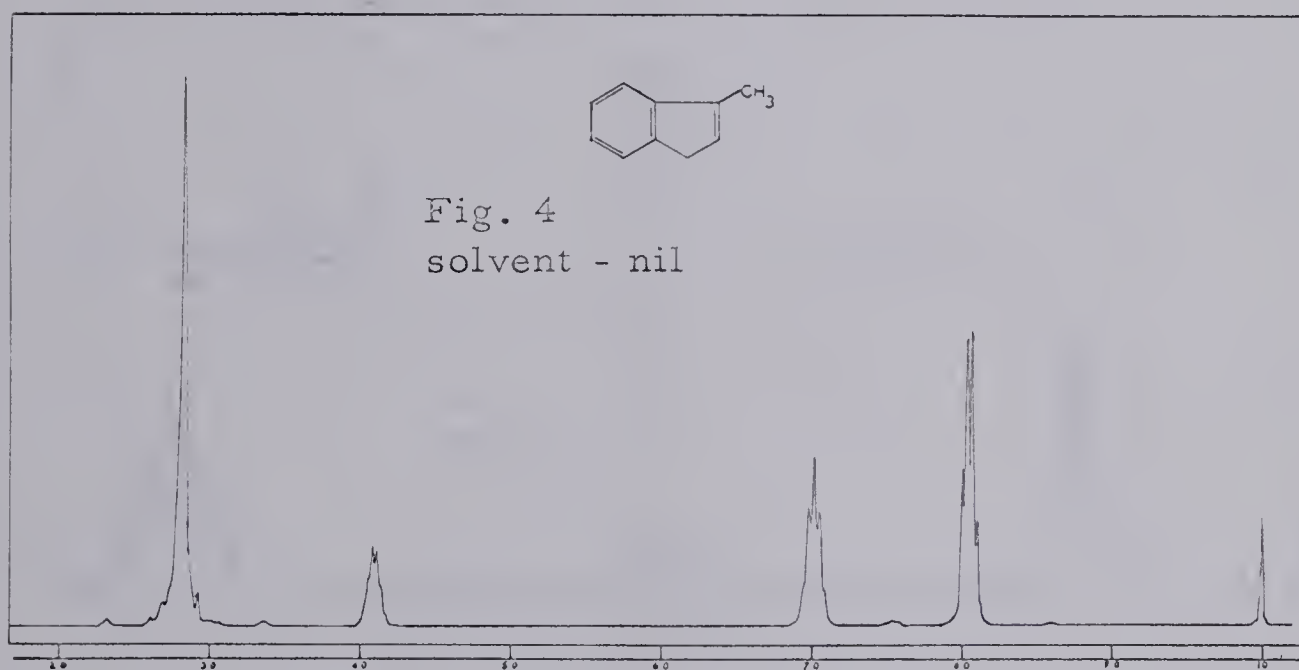
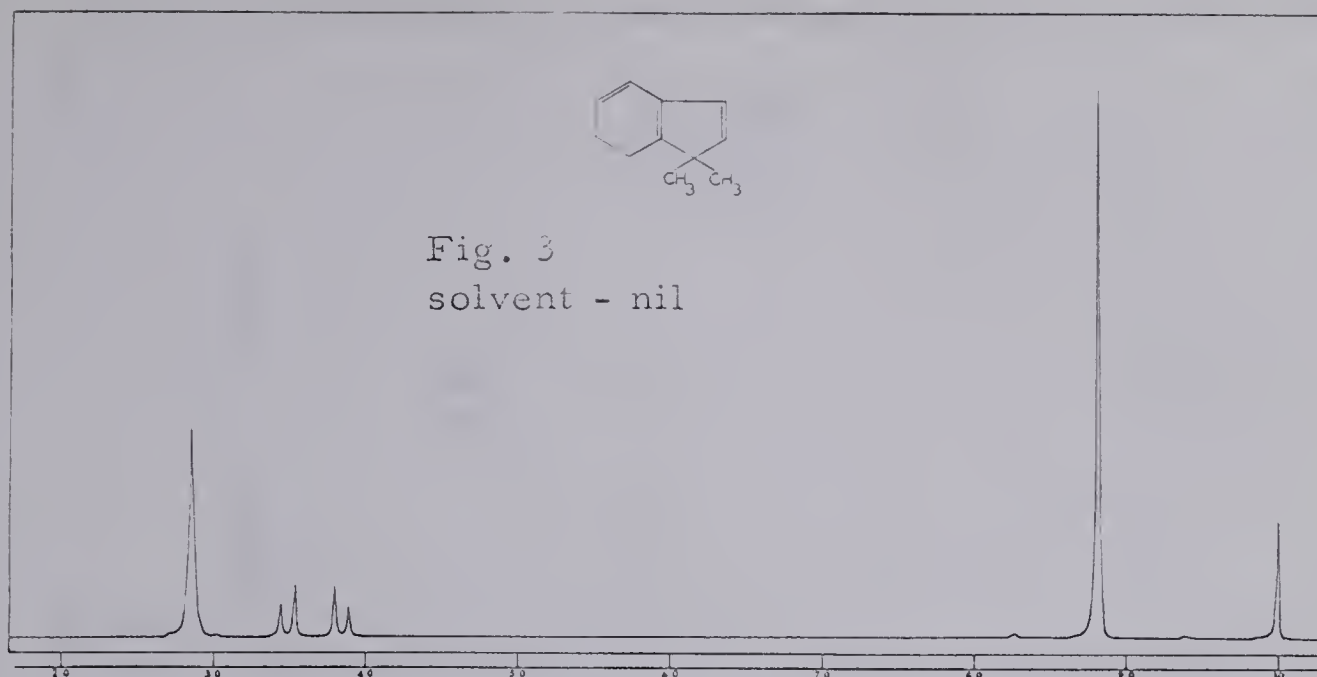
formed during the reactions. Starting with 7.71 gm (0.05 mole) of acenaphthene, elution with Skellysolve B gave 6.3 and 6.6 gm. of hydrocarbon mixture when one equivalent of potassium and lithium was used respectively. Ether-methyl alcohol elutions gave an additional 1.37 and 1.15 gm of a viscous oil for these two cases. That extensive methylation occurred when two equivalents of potassium were employed was indicated by the fact that 7.6 gm of reaction products could be eluted with Skellysolve B as compared with approximately 6.1 gm for the metalation reaction when no methyl iodide was introduced (see p. 136). In addition to the above 7.6 gm of products obtained when Skellysolve was the eluant, 0.86 gm of polymeric material was recovered with ether-methyl alcohol elution. Total recoverable material in these experiments varied in weight therefore between 7.6 and nearly 8.5 gm.



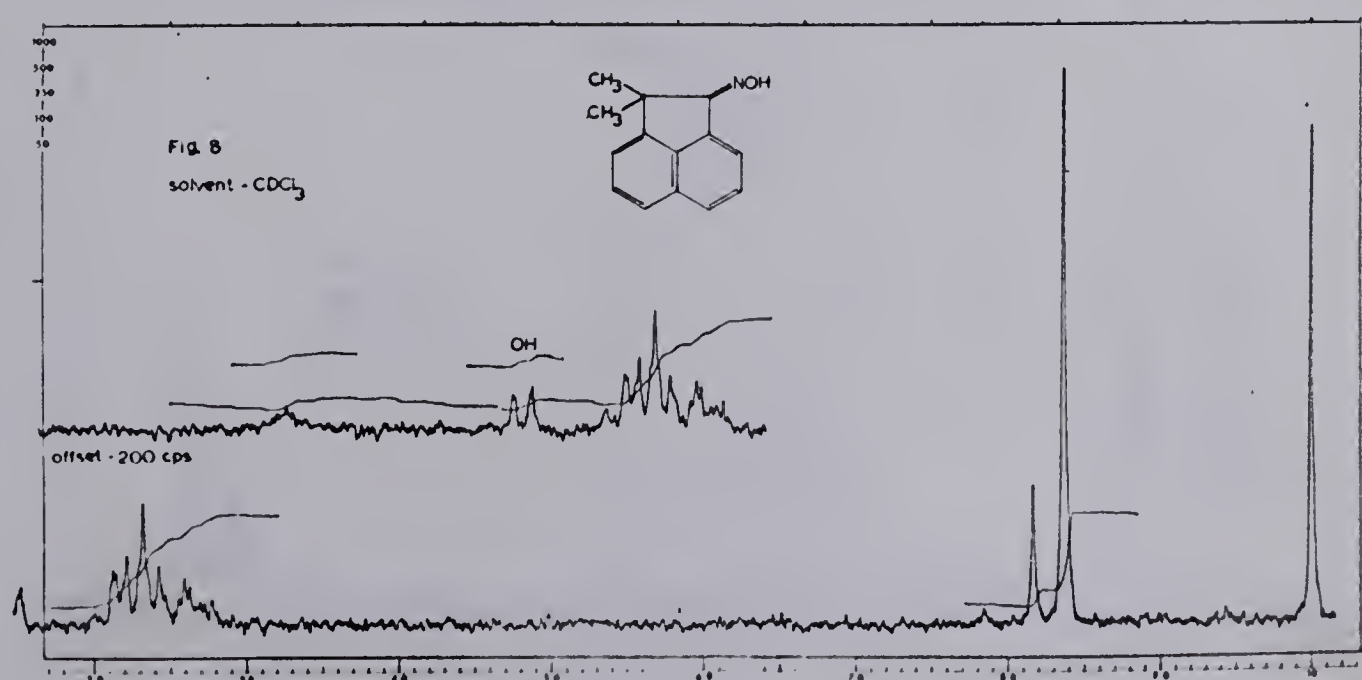
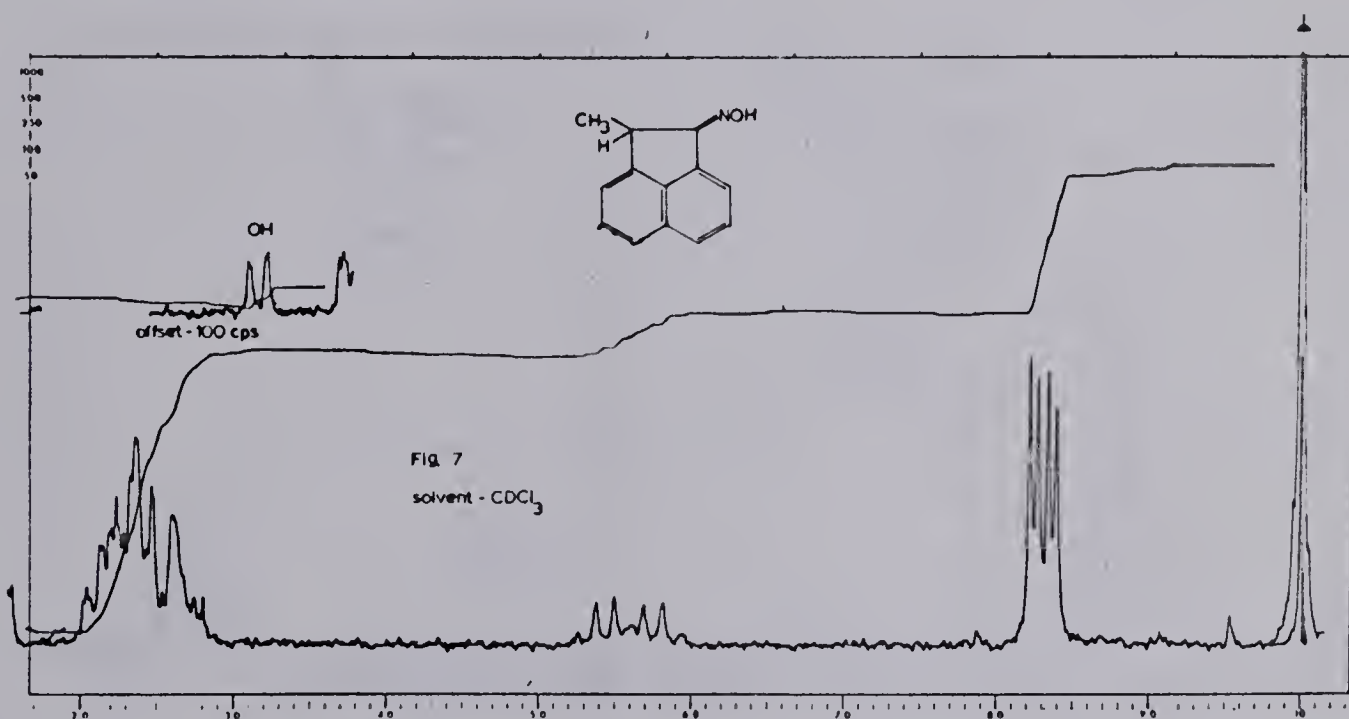
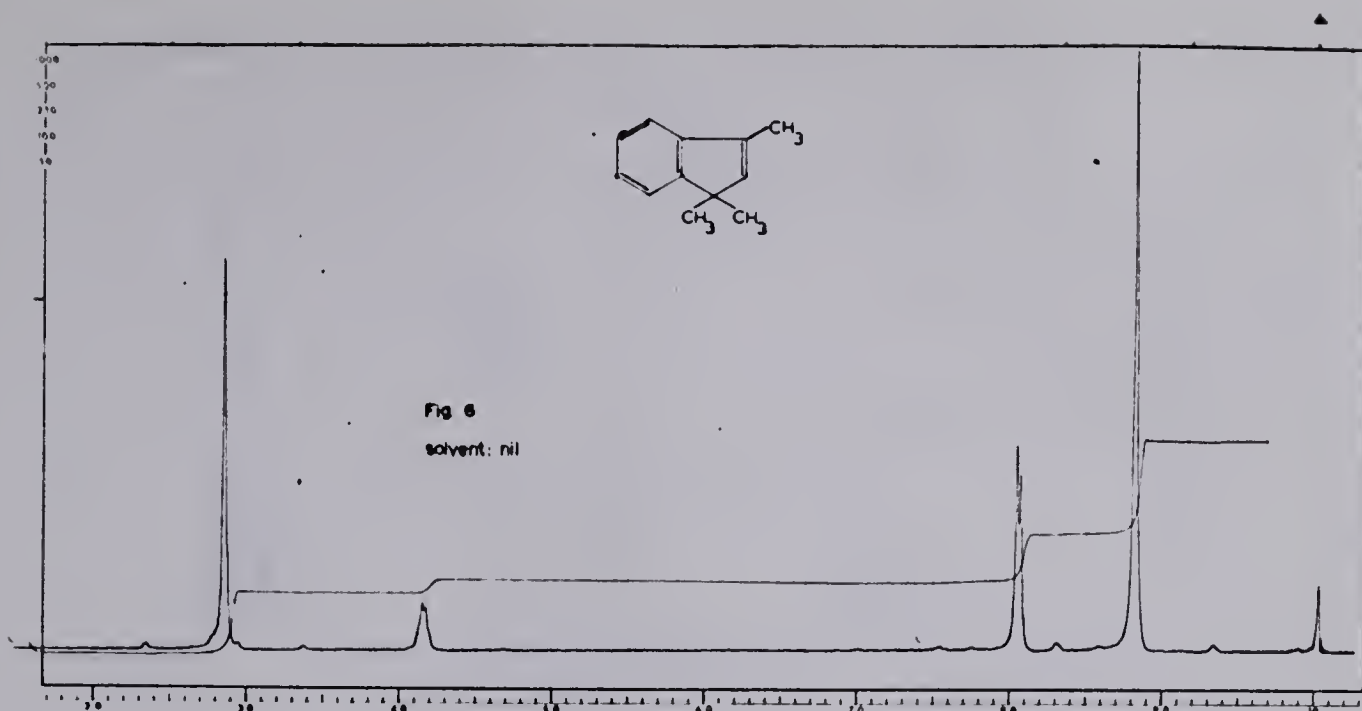
On p. 143-156 all the NMR, IR, and UV spectra mentioned in the Discussion and the Experimental can be found. All NMR spectra are referred to tetramethylsilane ( $\tau=10.00$ ) as the internal standard.



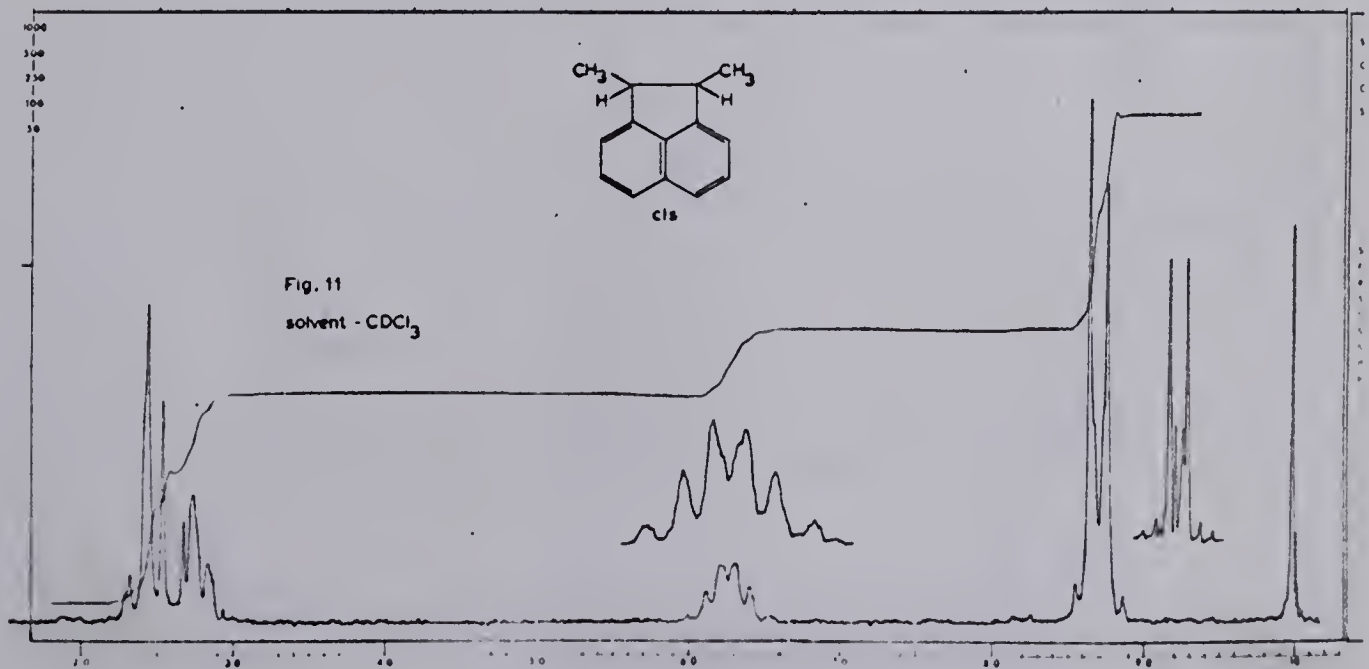
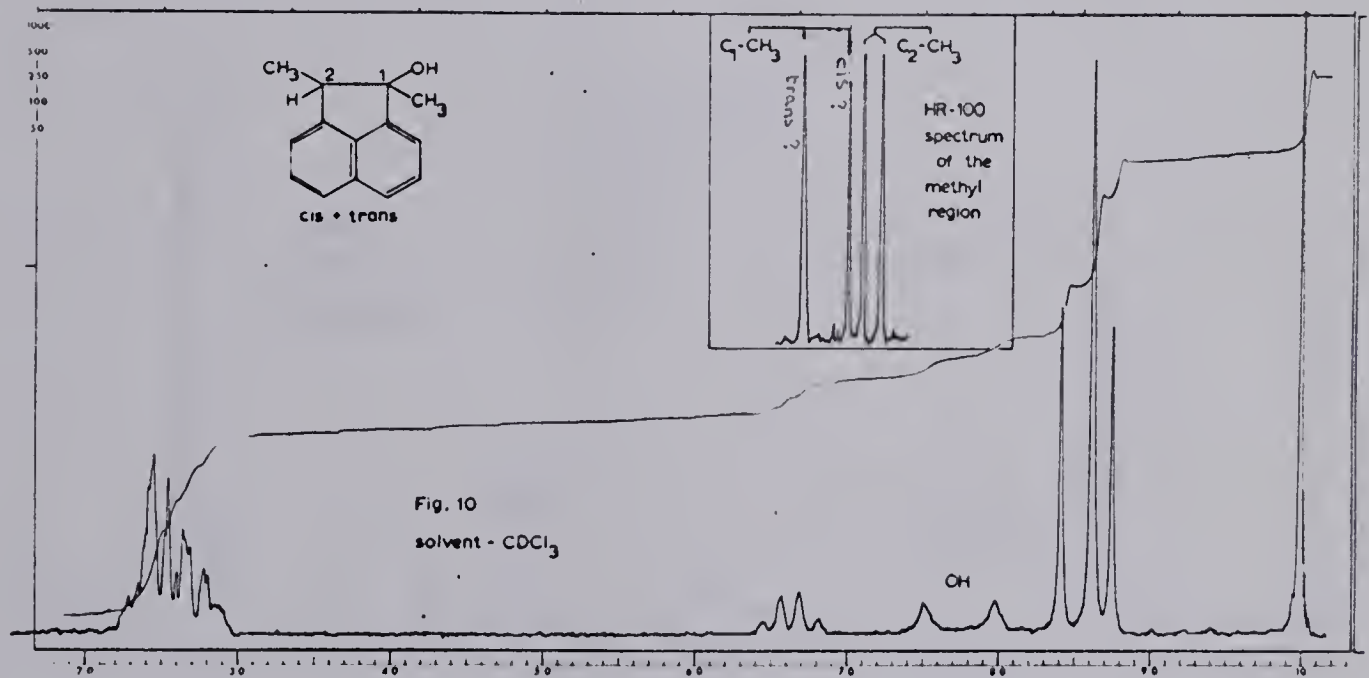
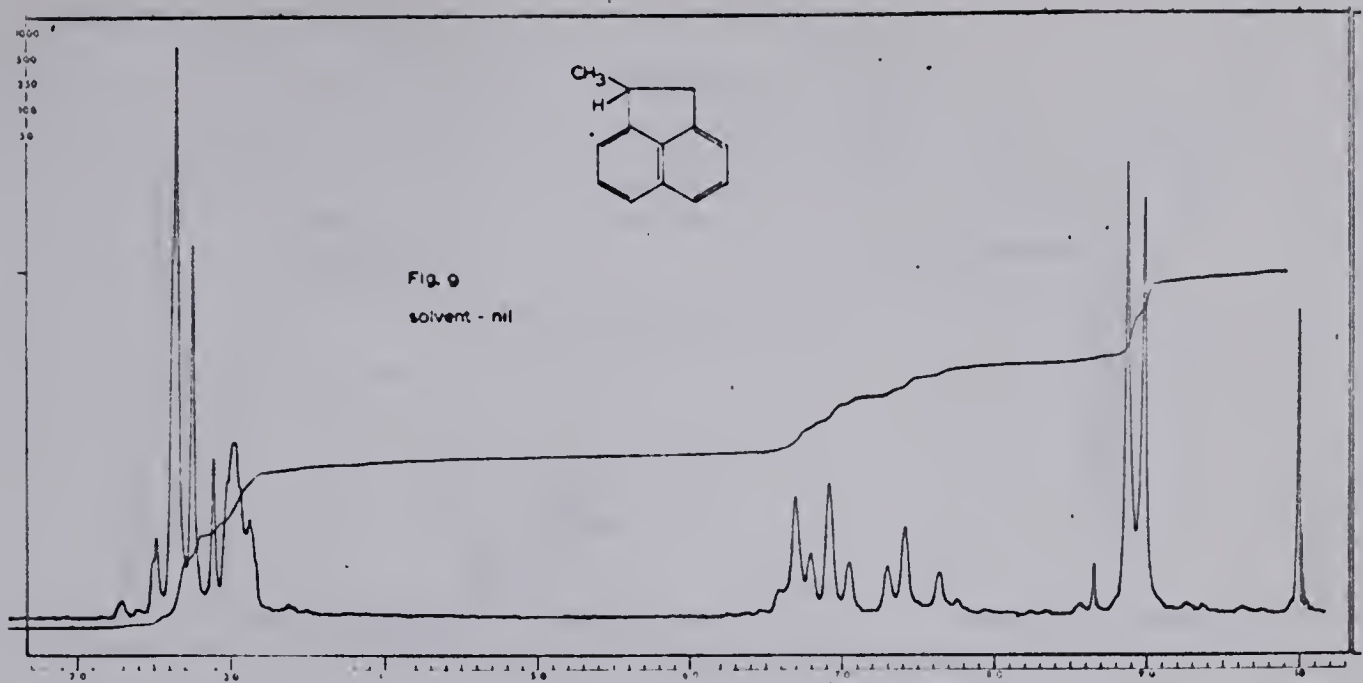




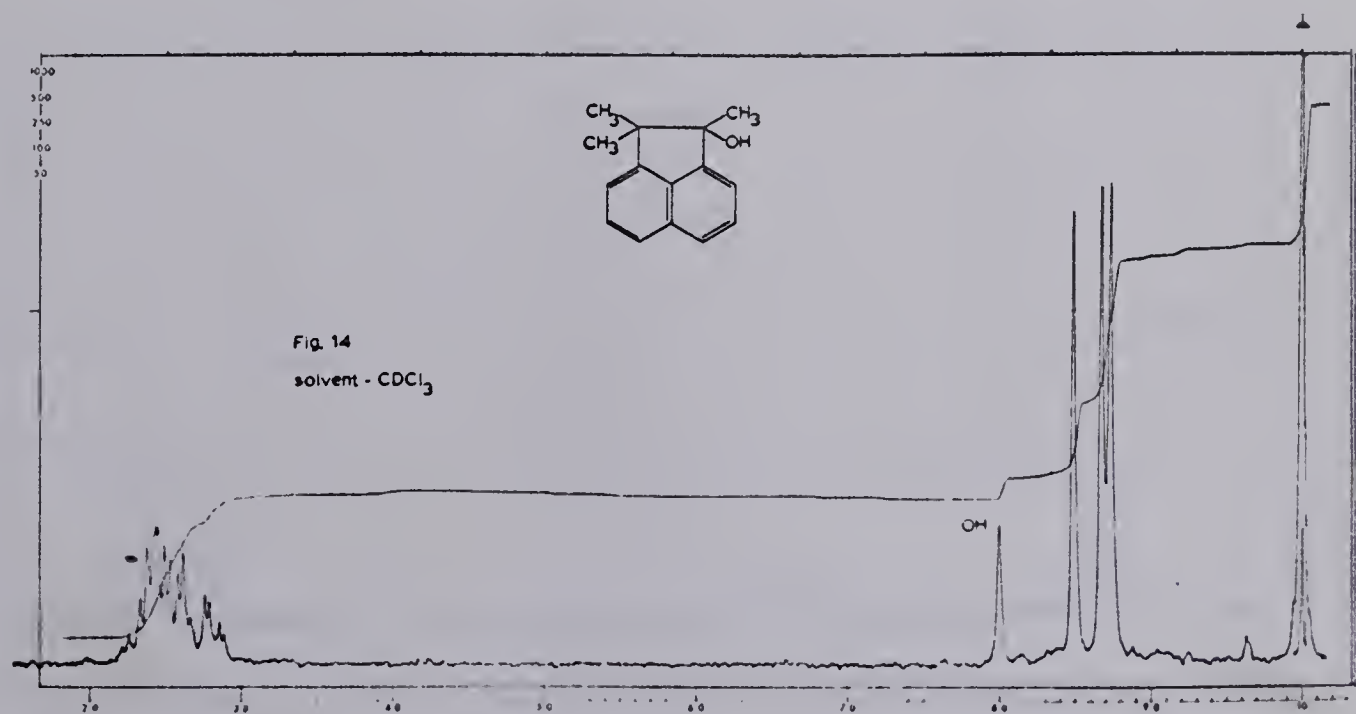
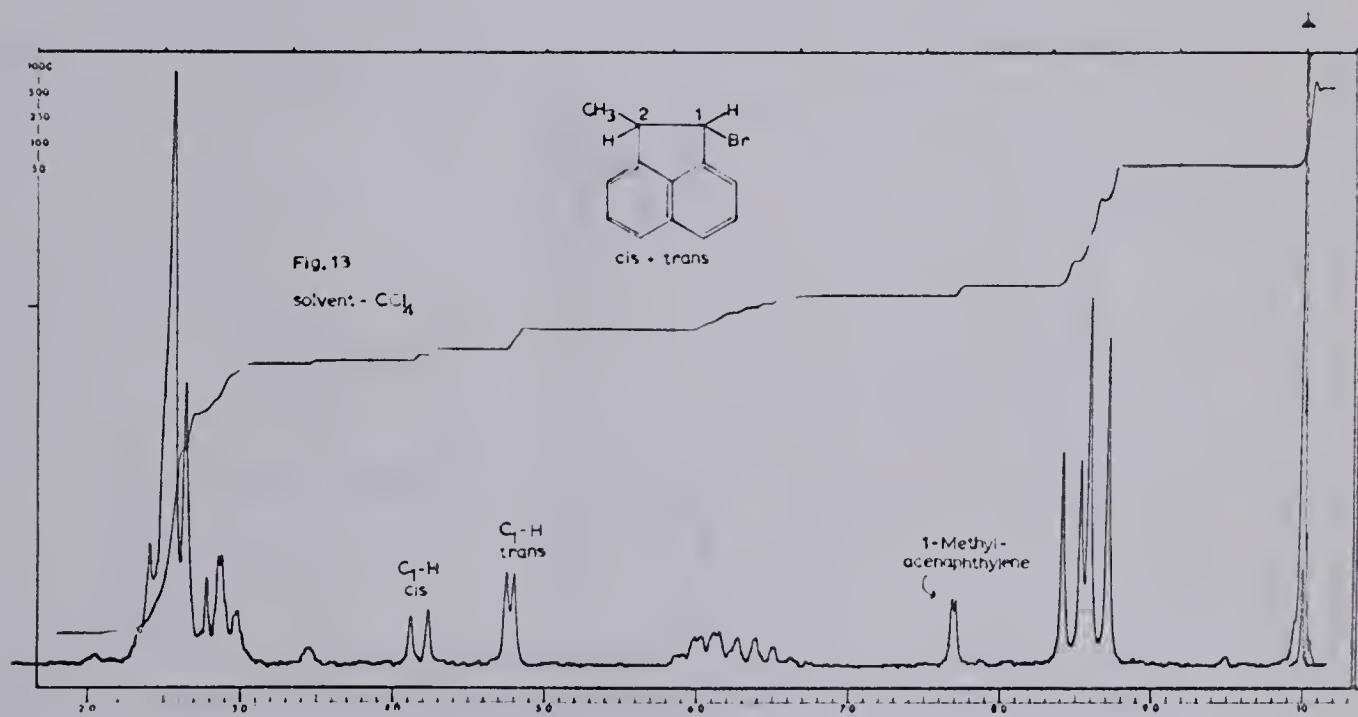
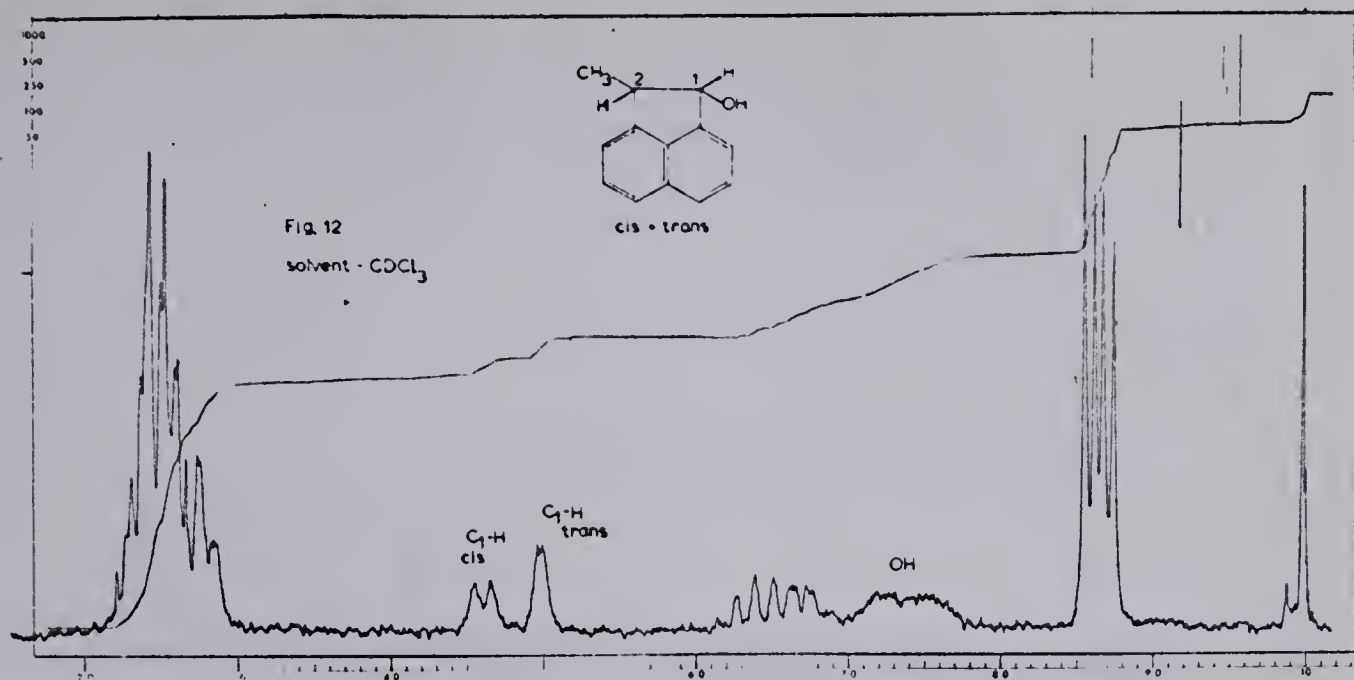




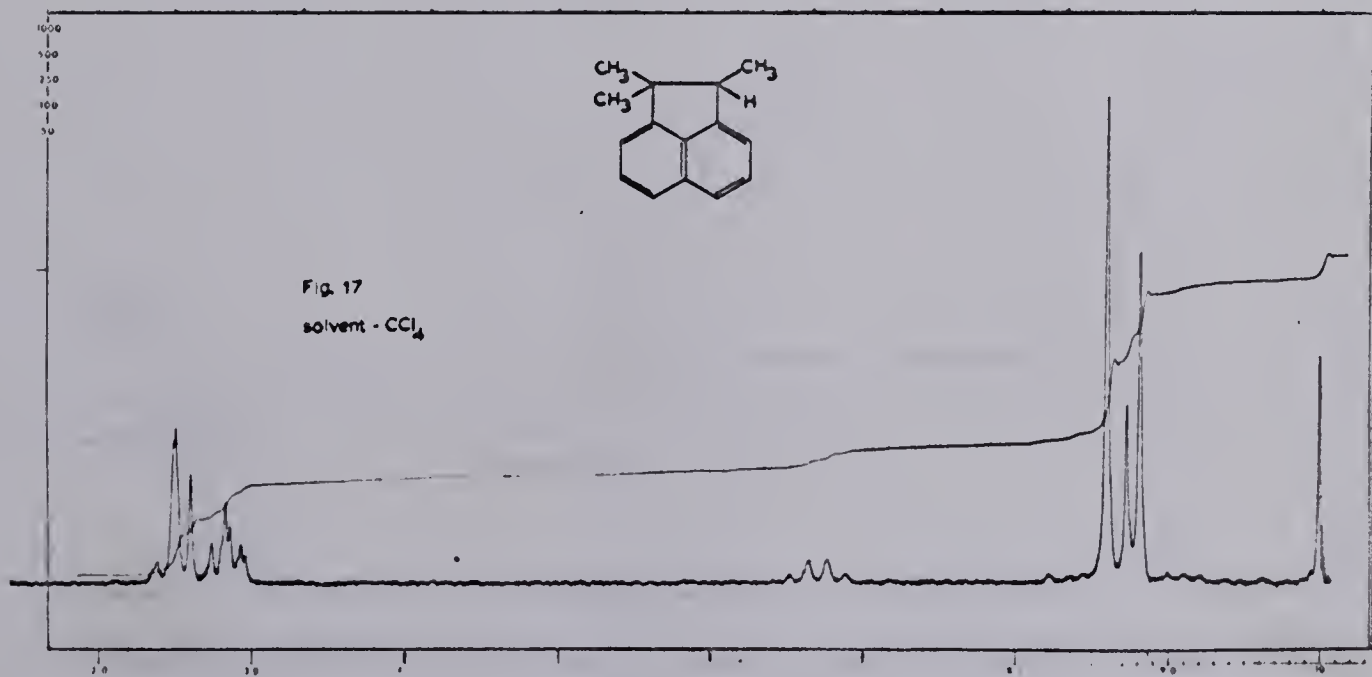
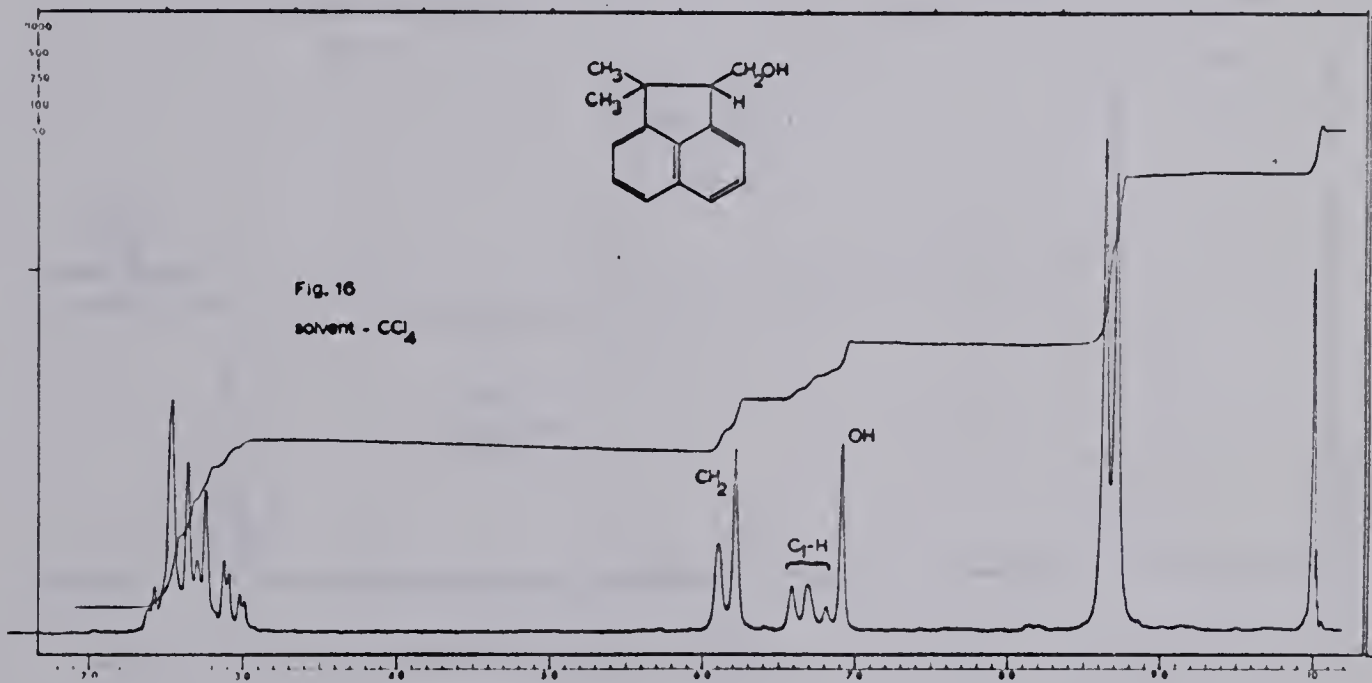
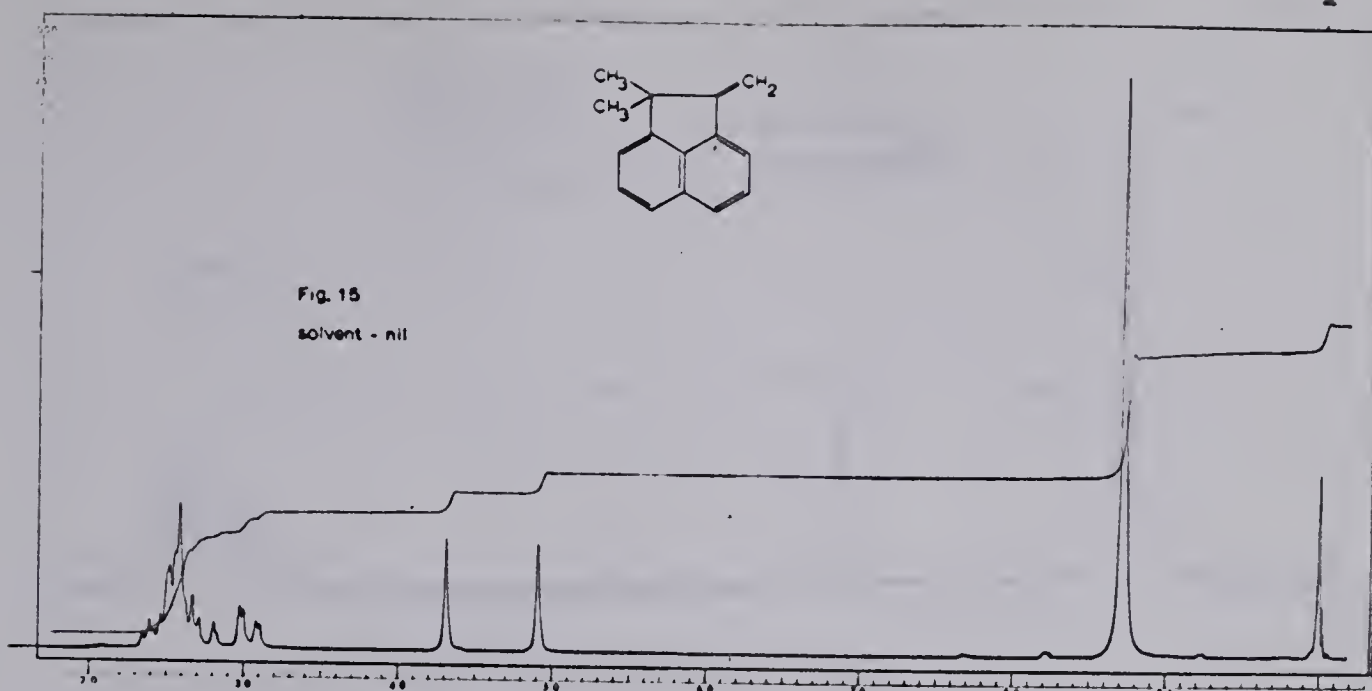




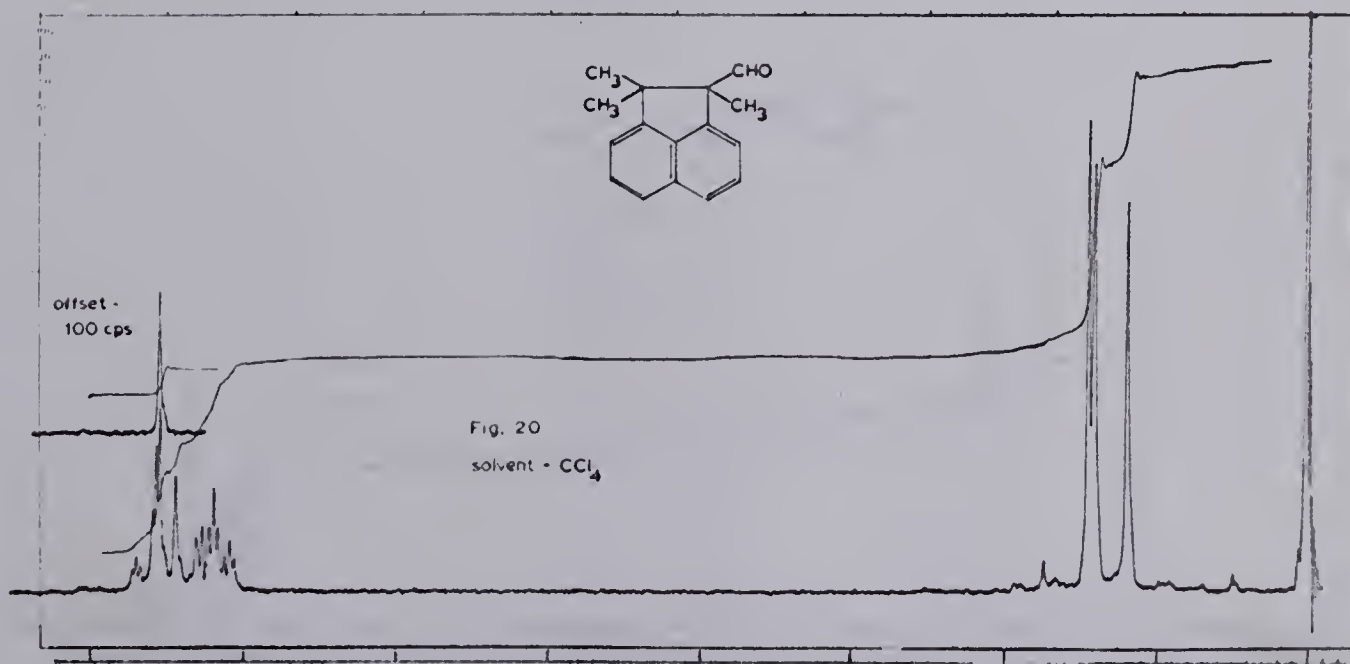
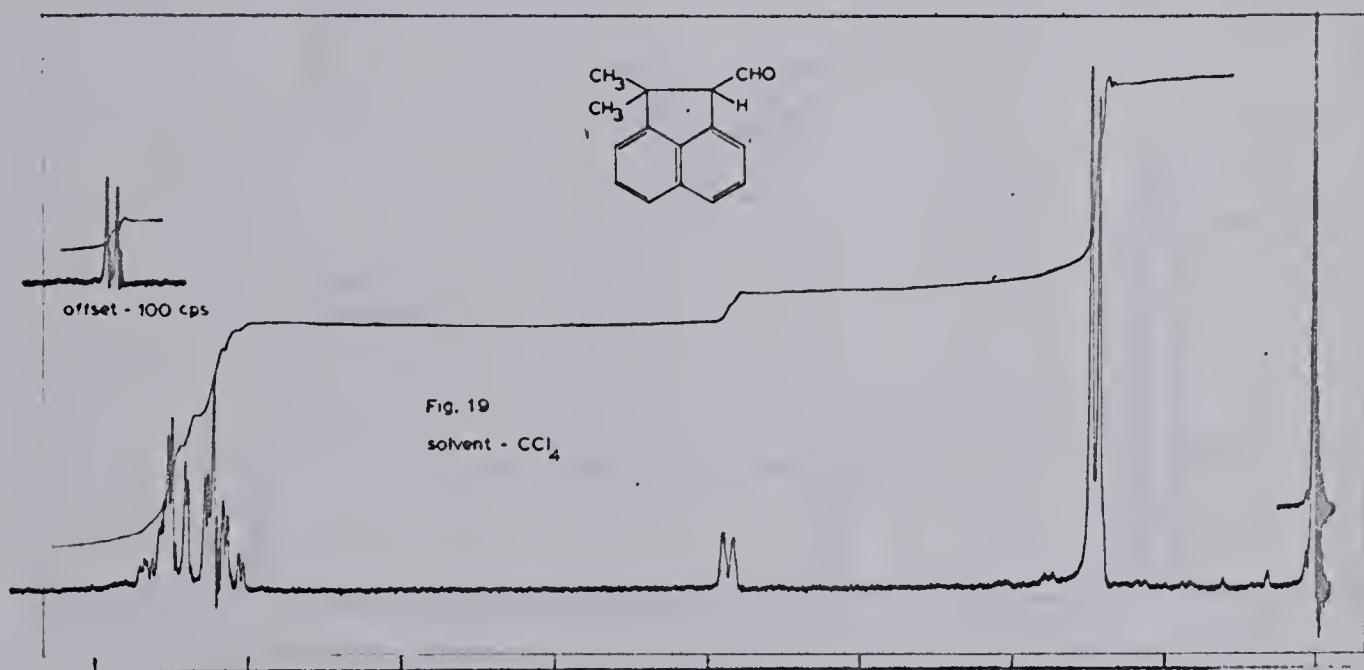
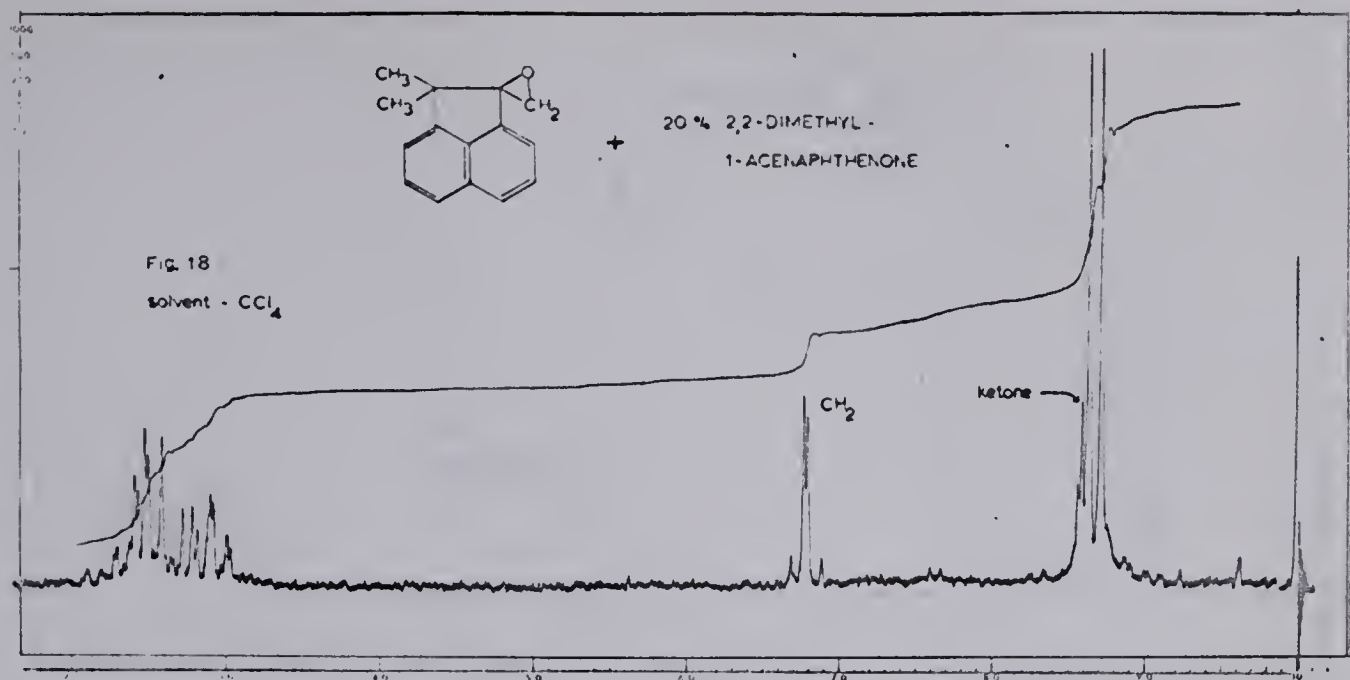




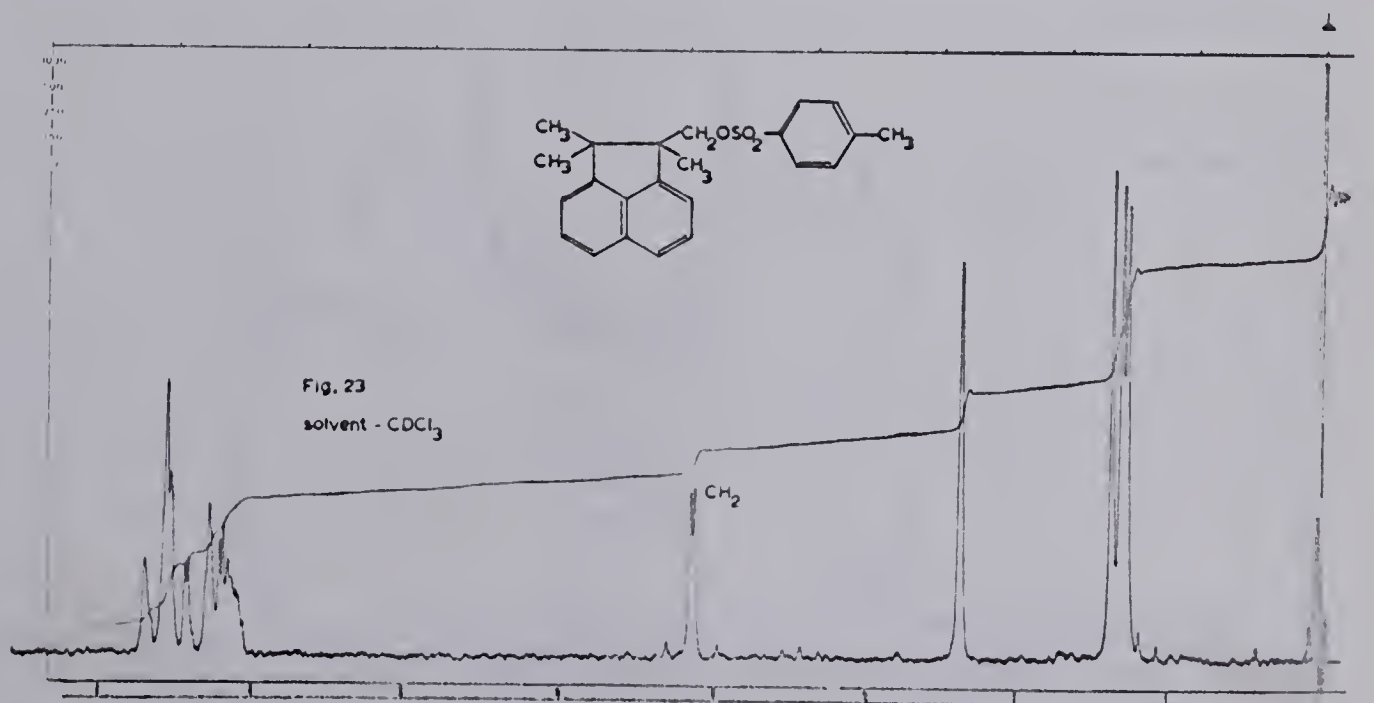
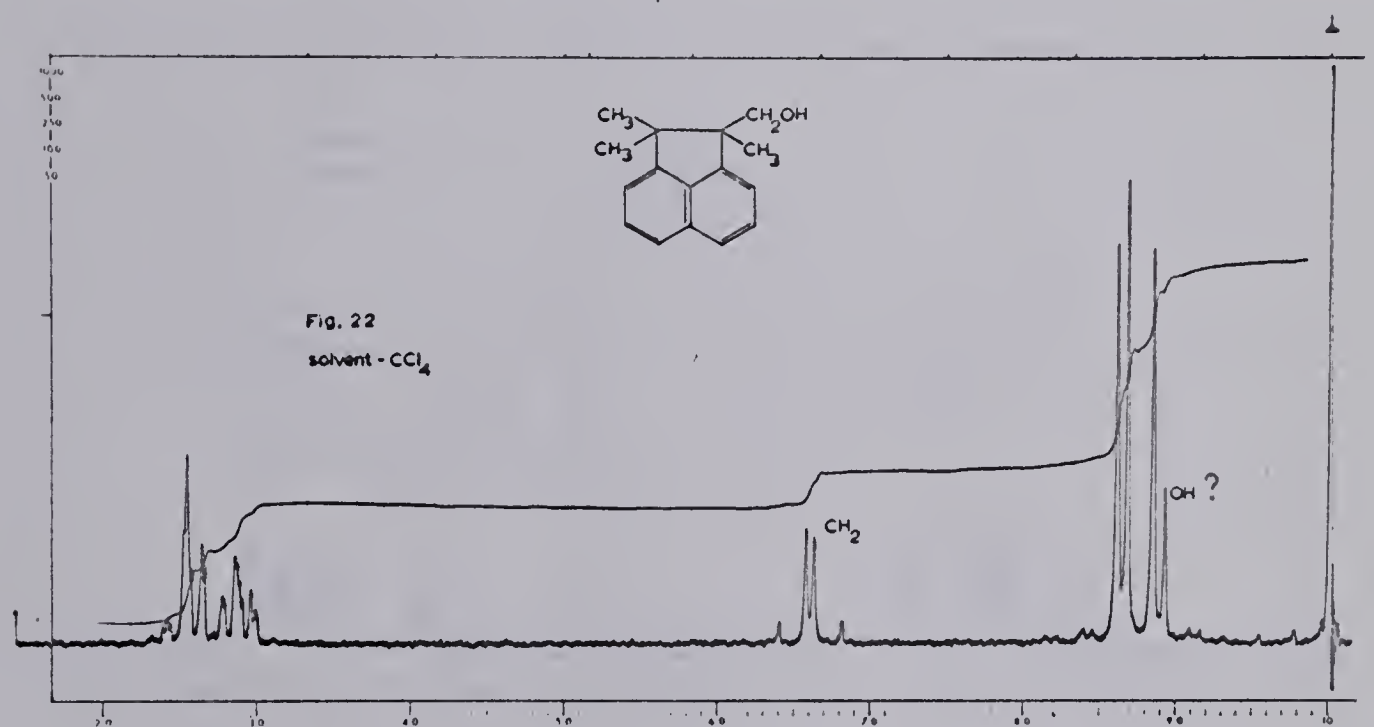
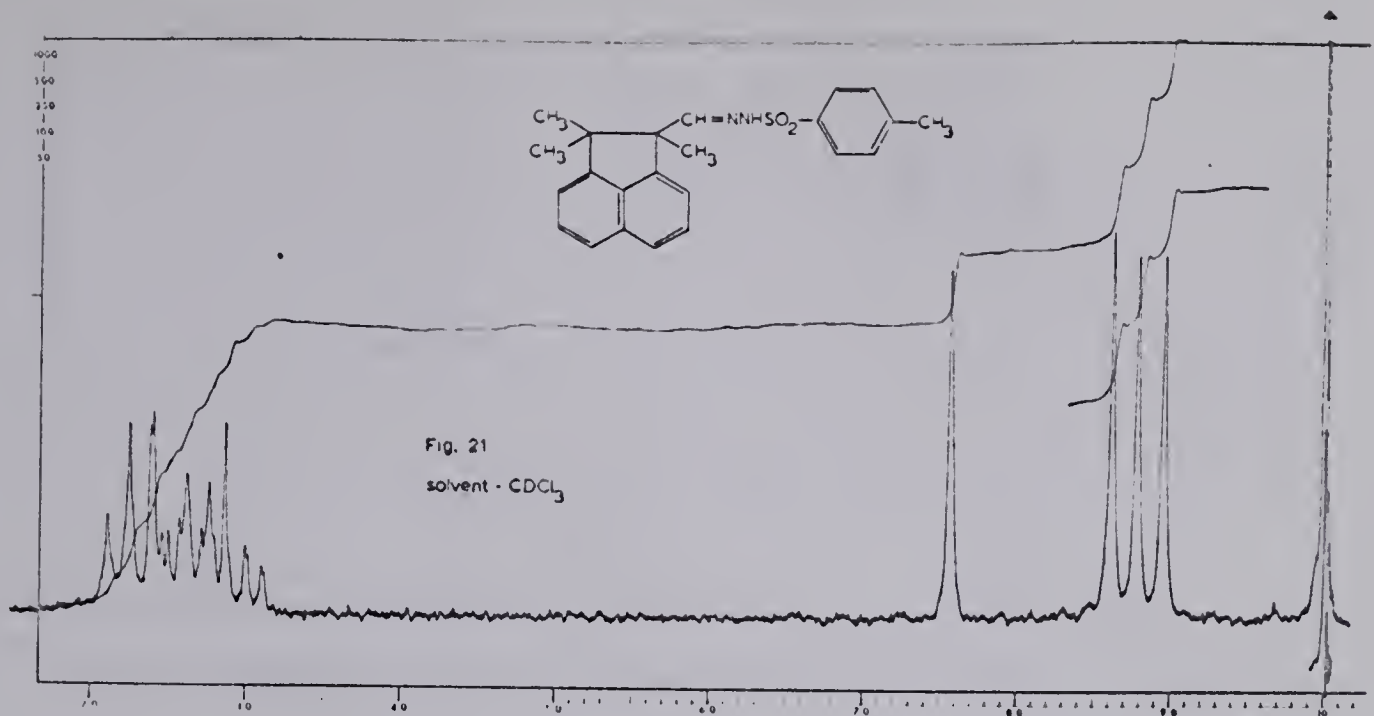




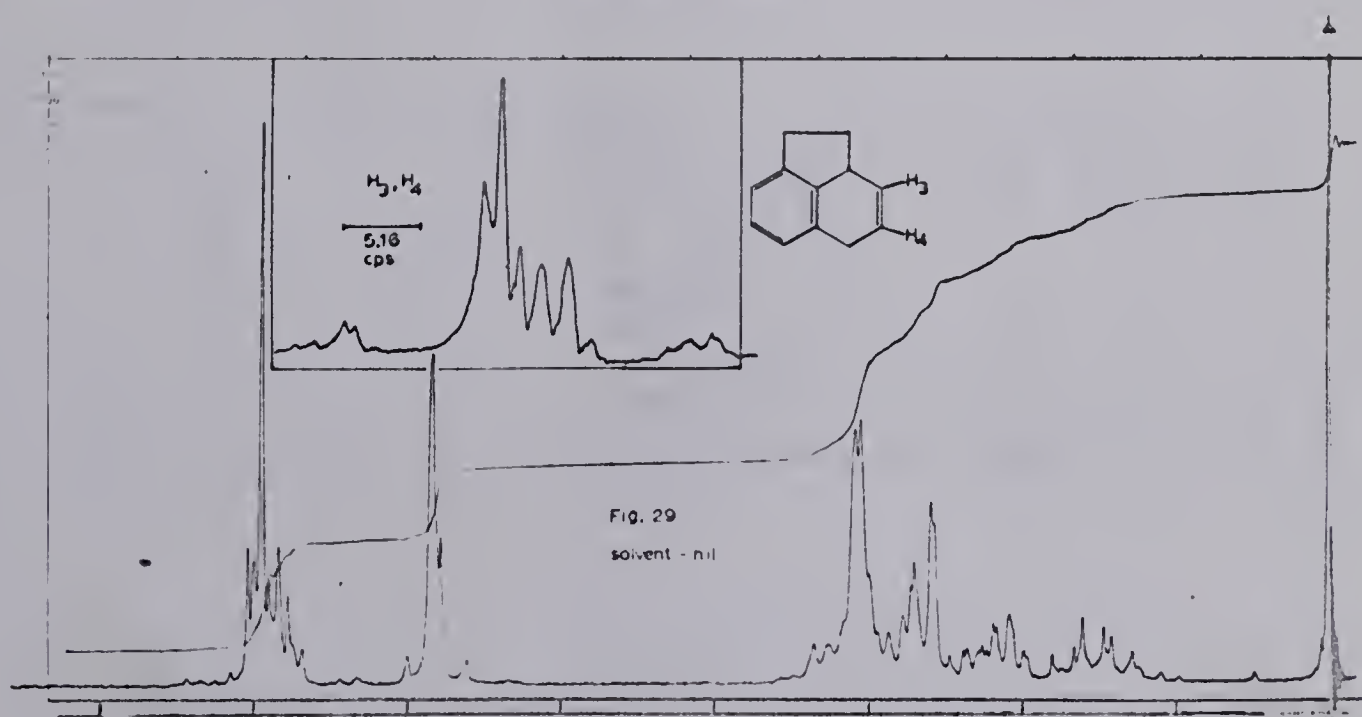
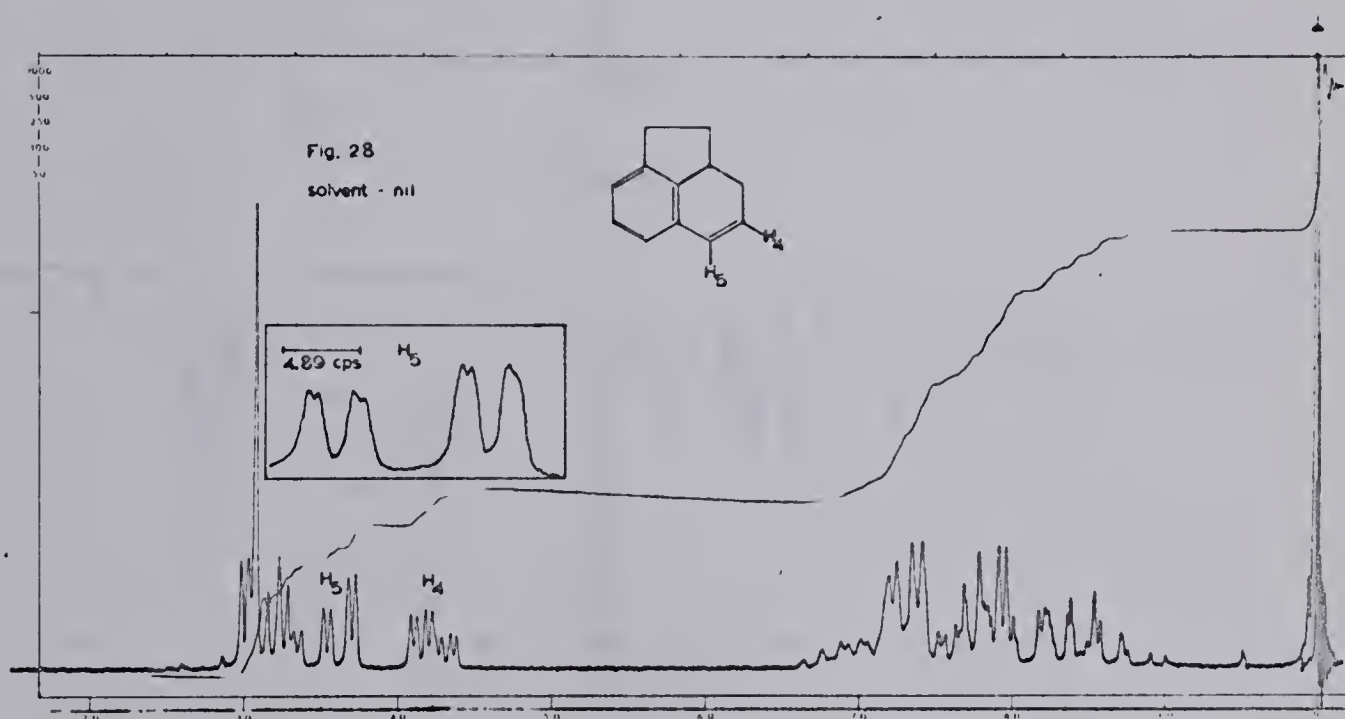
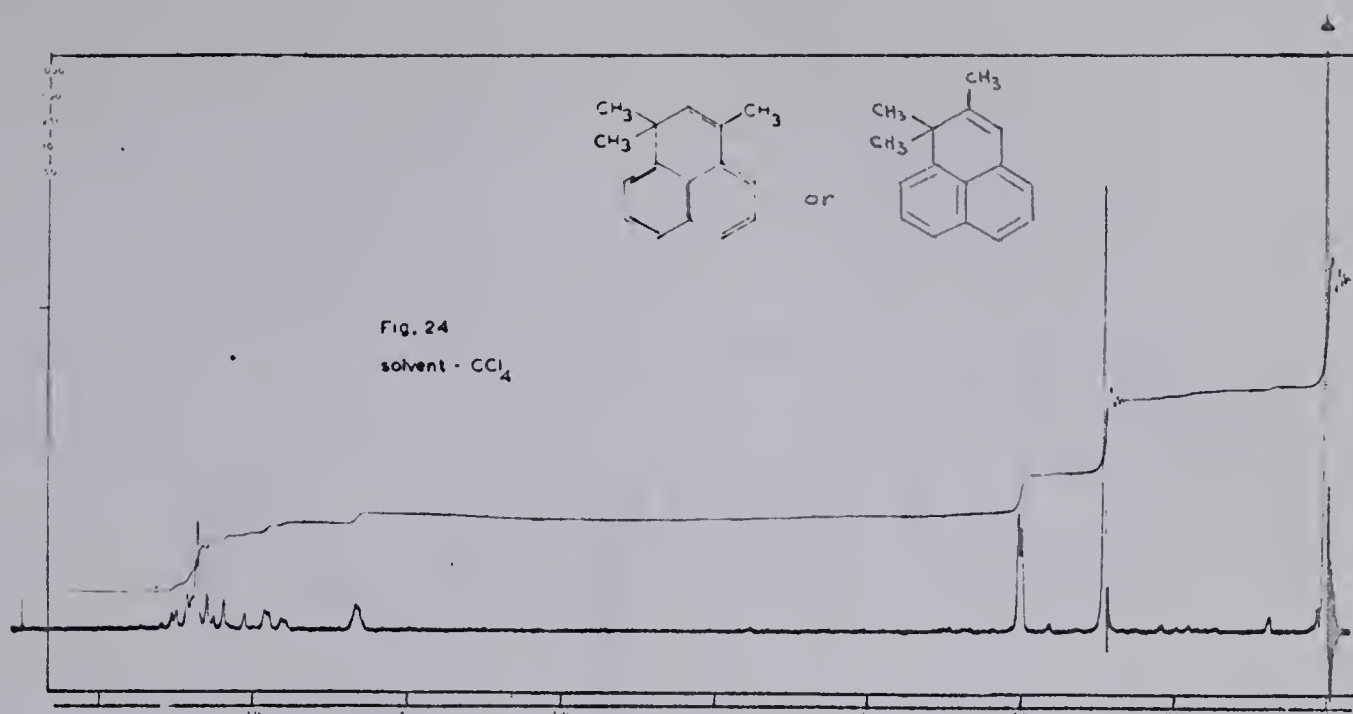




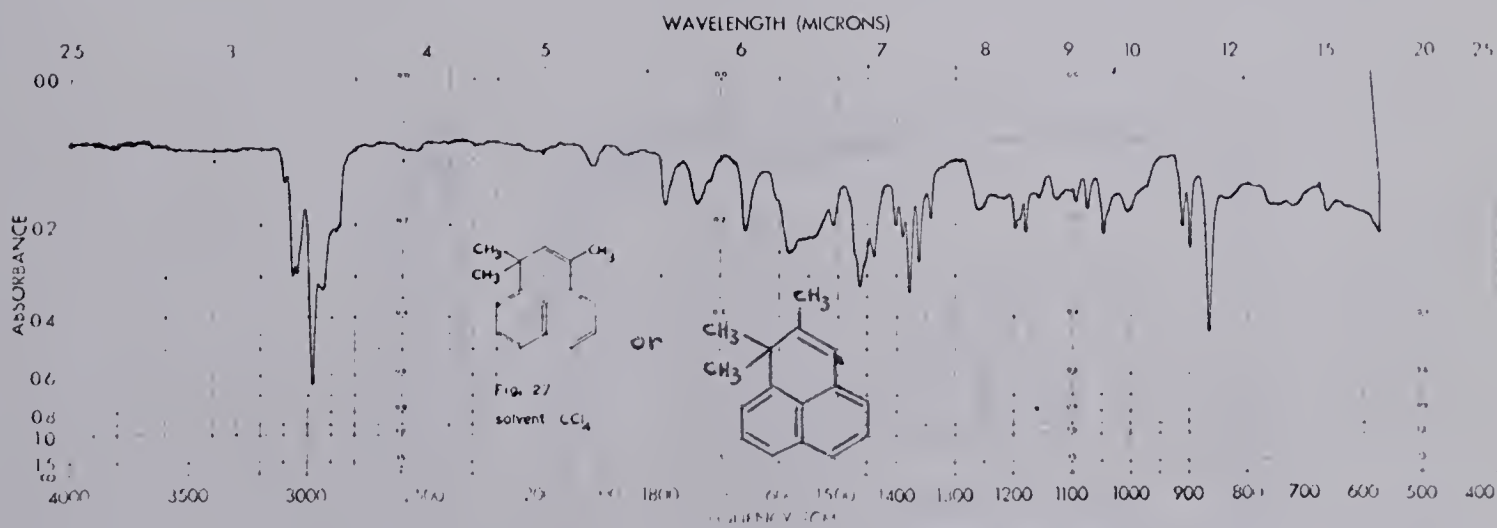
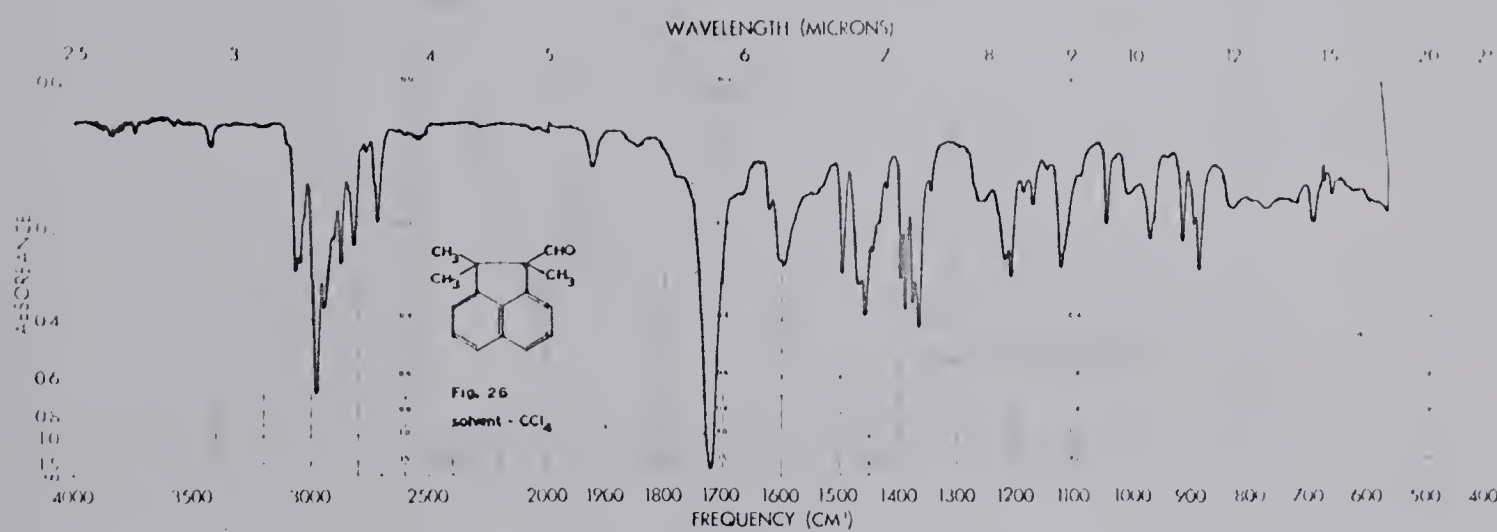
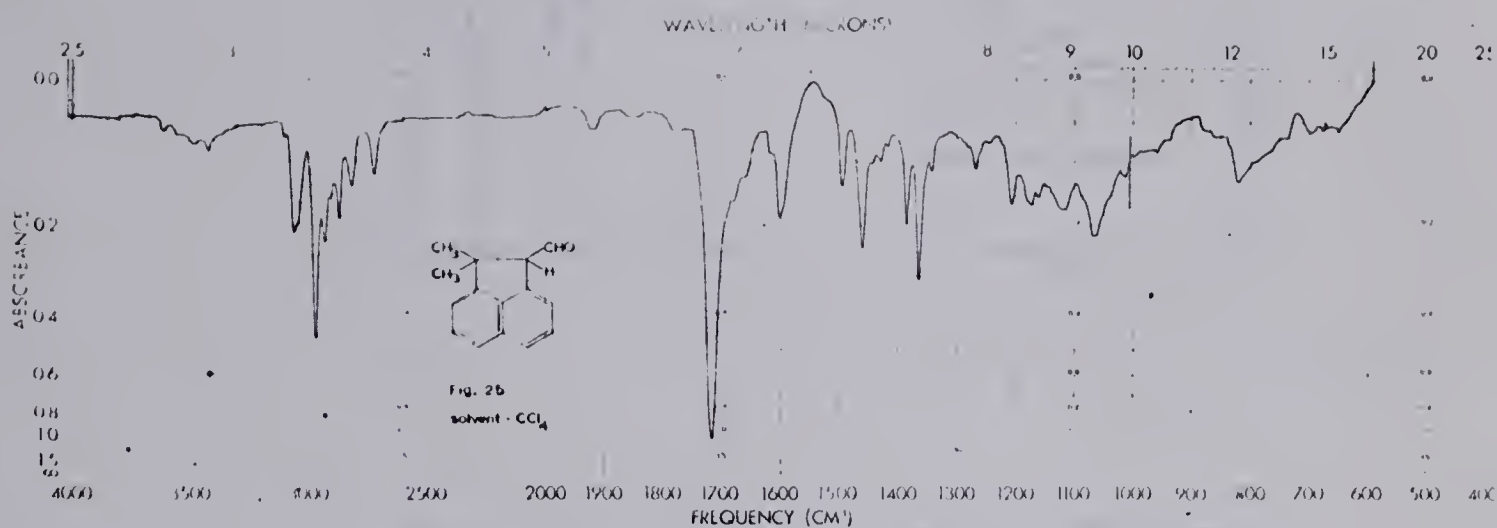




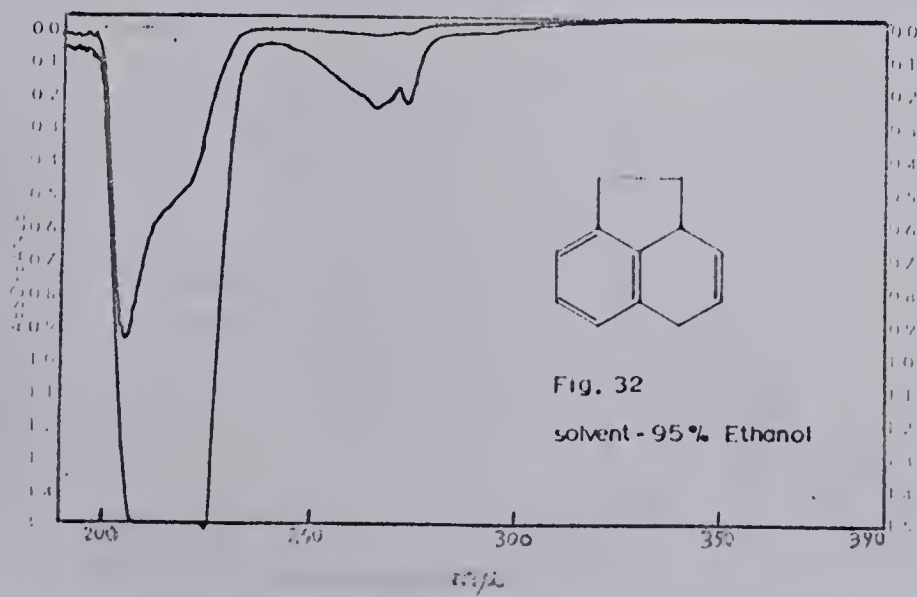
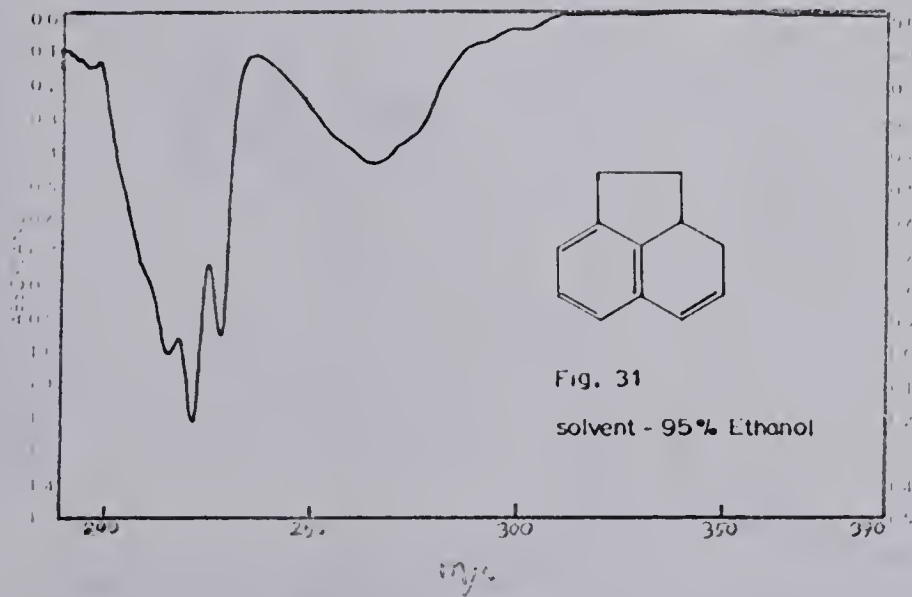
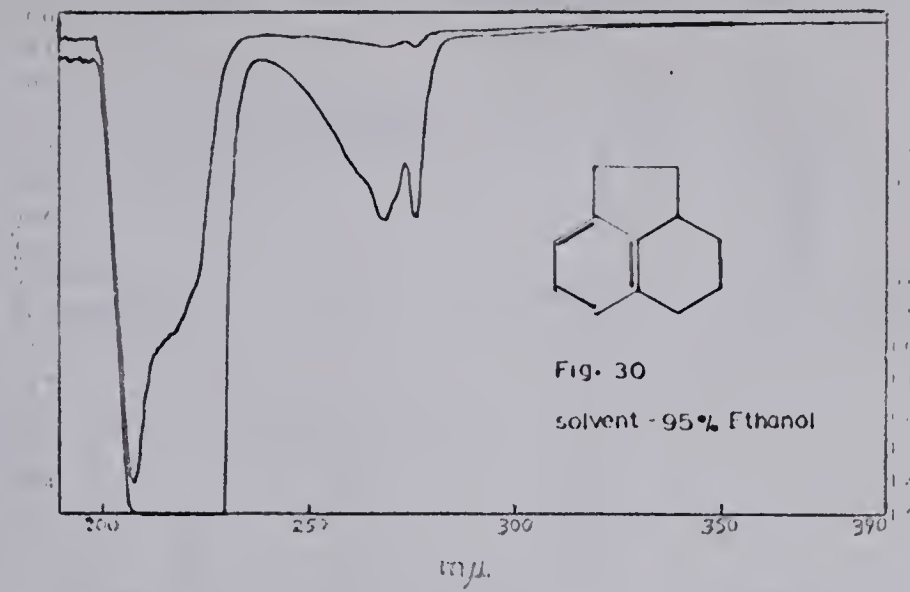




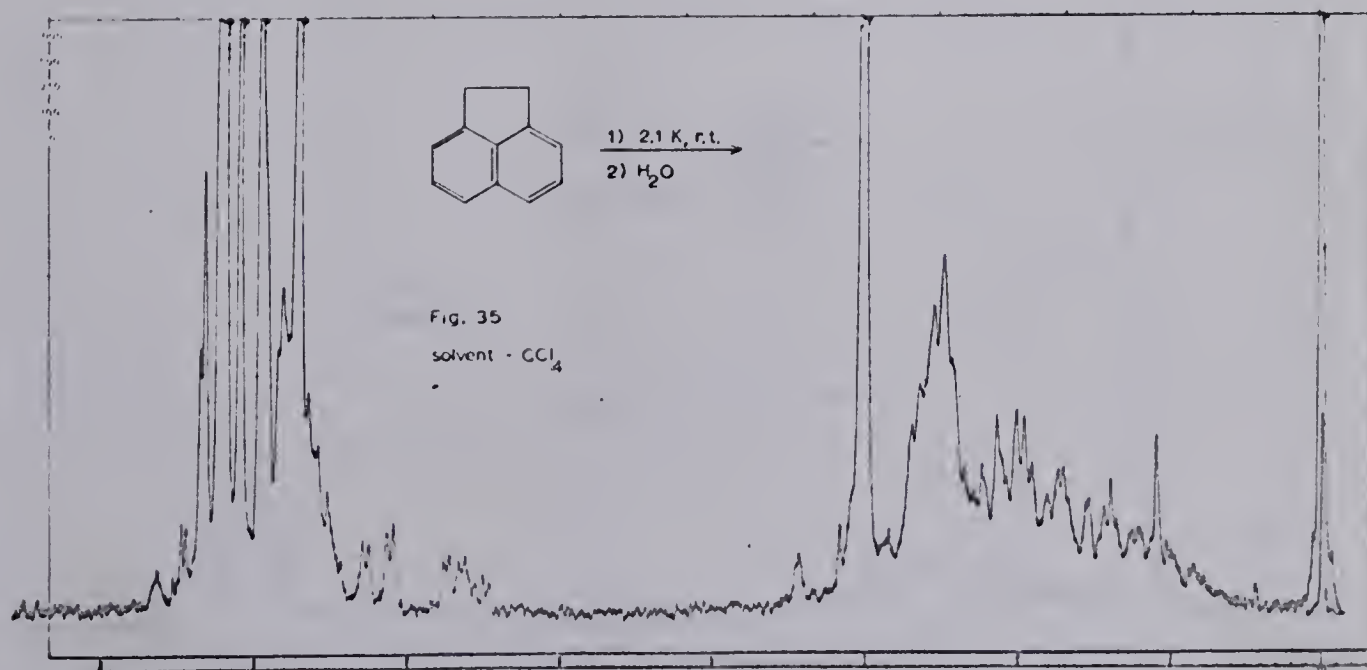
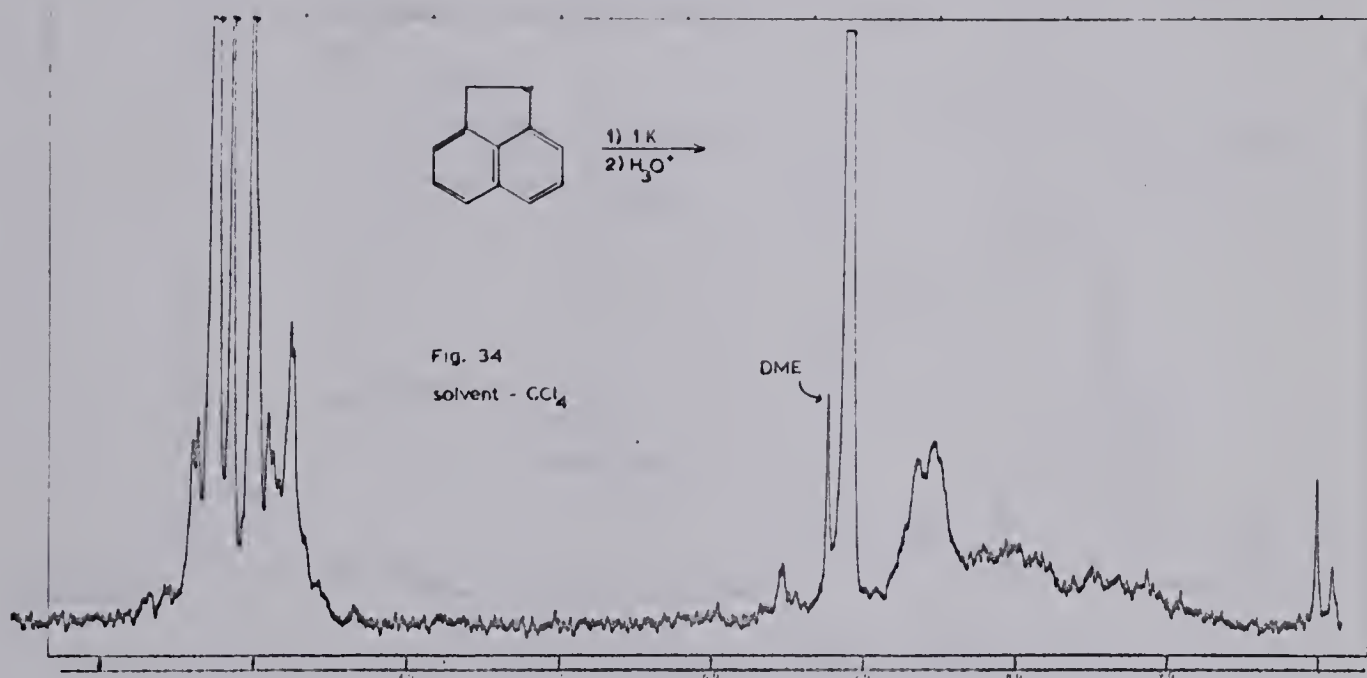
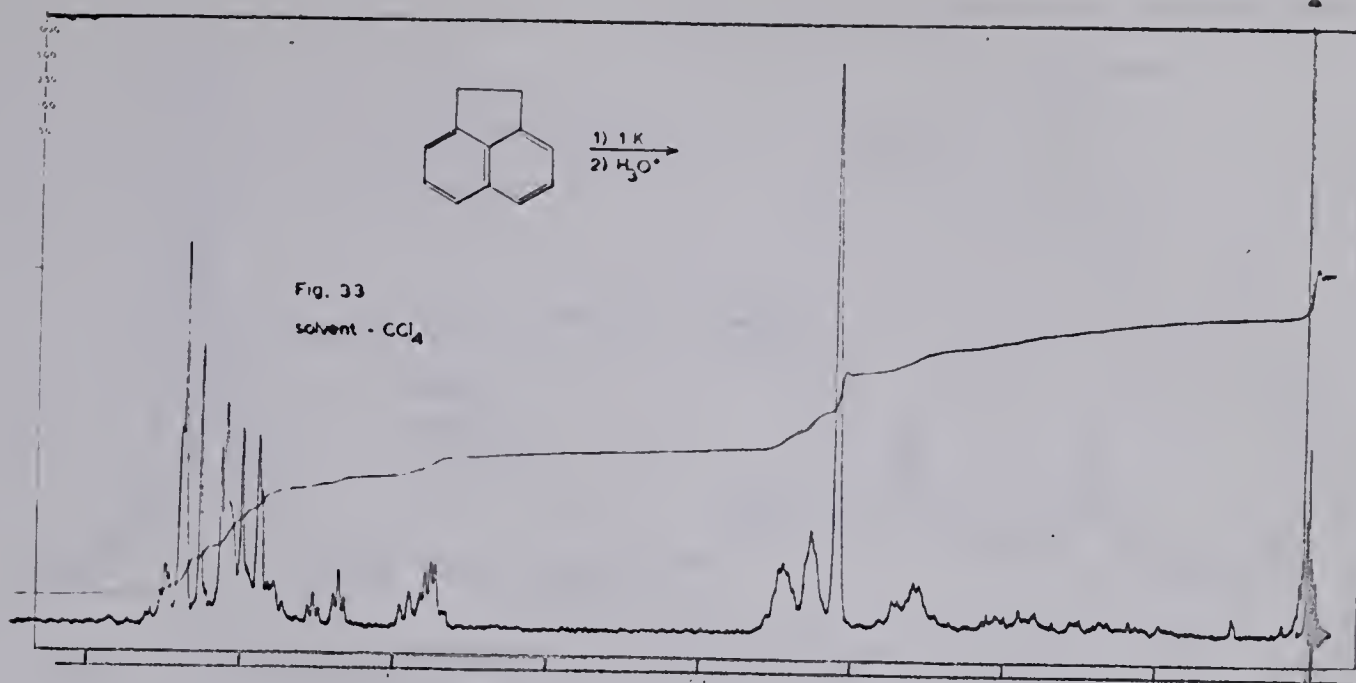




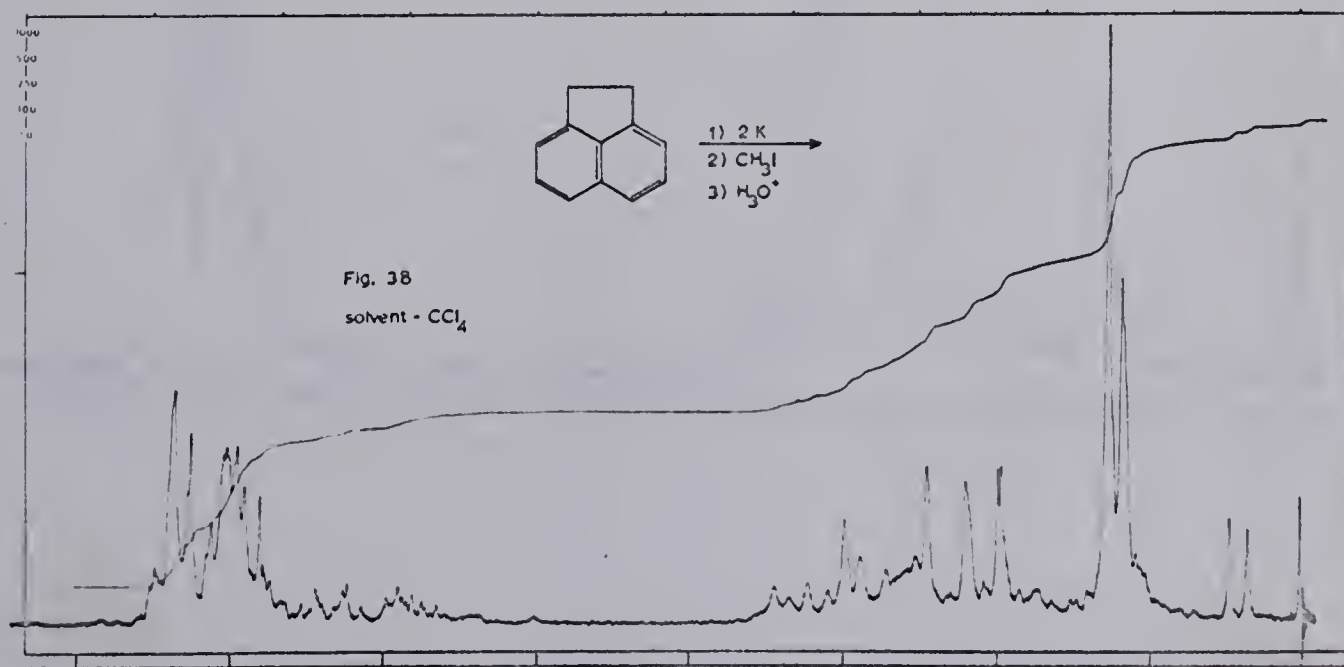
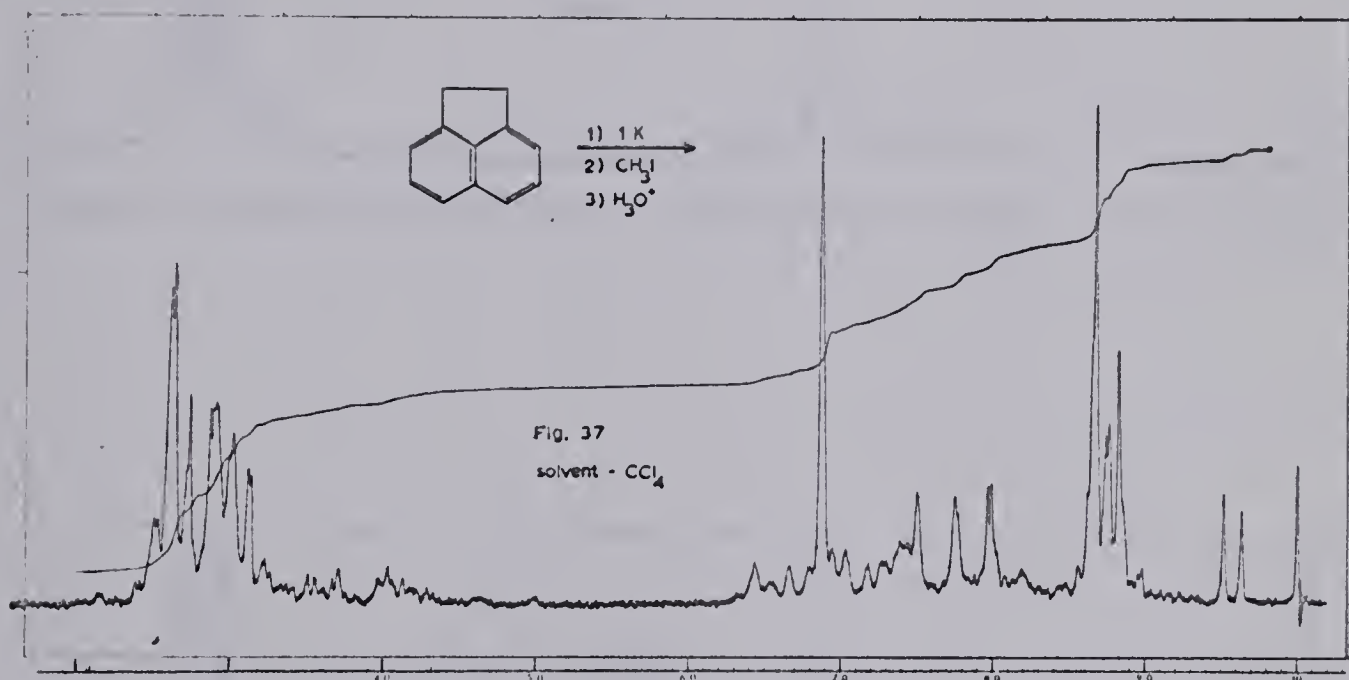
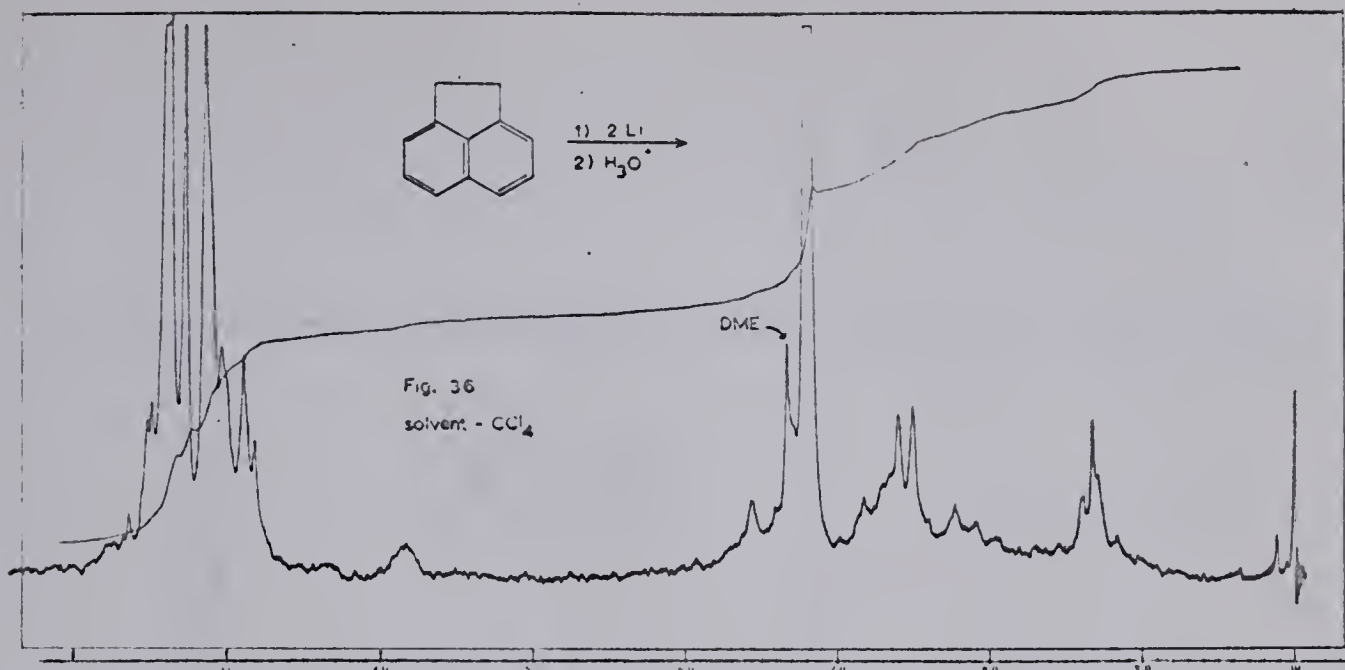




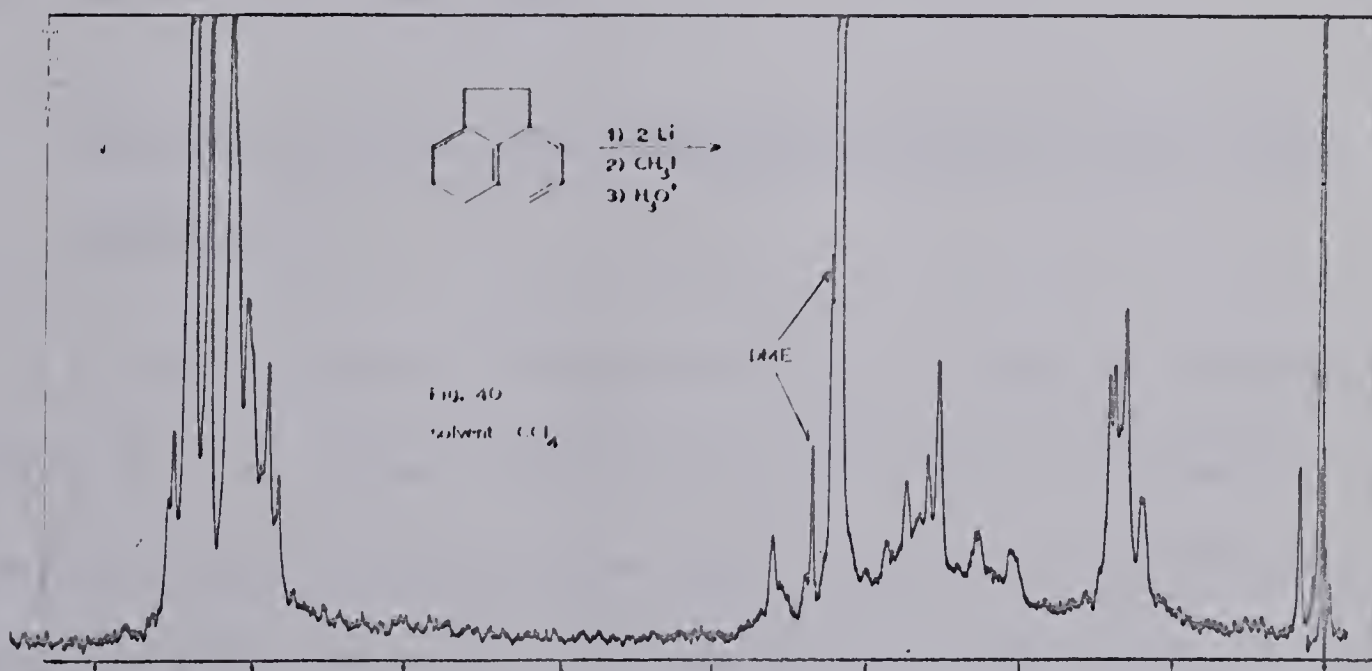
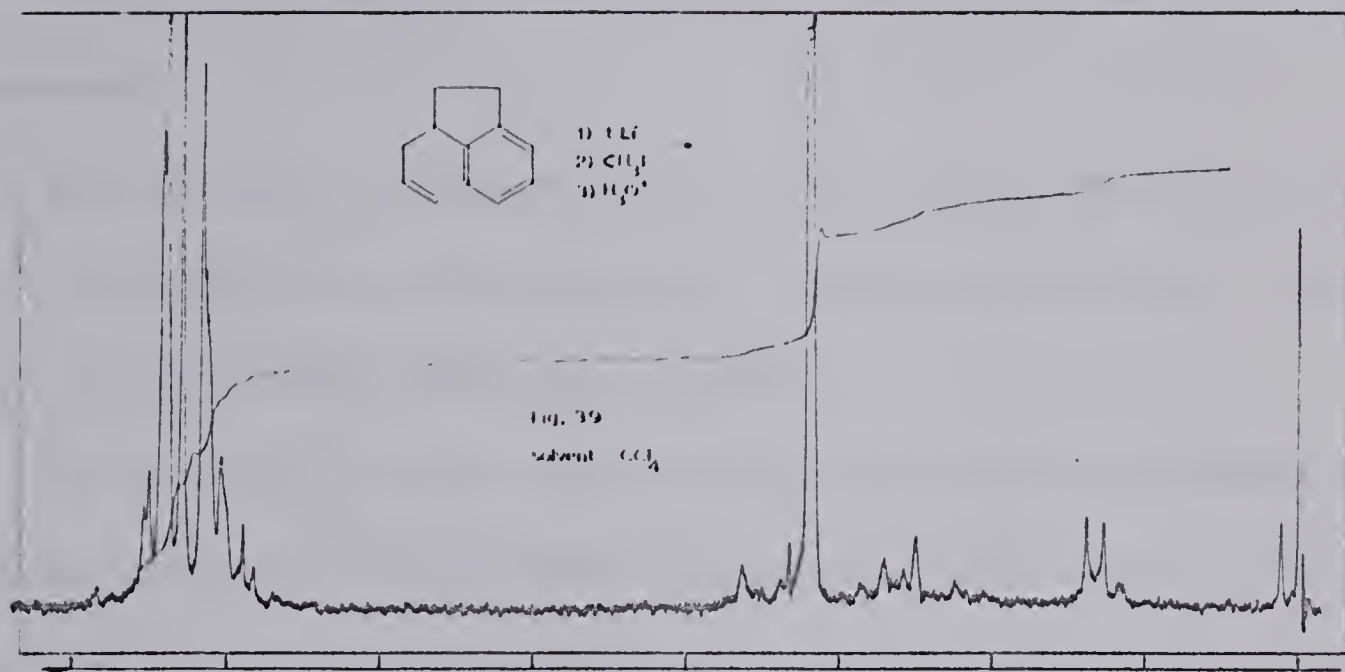














## EXPERIMENTAL

All melting points and boiling points reported in this section are uncorrected.

Microanalyses were performed by Miss Darlene Roberts of the microanalytical section of the Chemistry Department, and by C. Daessle Organic Microanalyses, Montreal, Canada.

Infrared spectra were recorded with a Perkin-Elmer Model 421 spectrophotometer, and ultraviolet spectra with a Perkin-Elmer 202 Ultraviolet-Visible spectrophotometer. Nuclear magnetic resonance spectra were recorded with Varian A-60 and HR-100 spectrometers. Mass spectra were obtained with a Metropolitan Vickers instrument, Model MS-2H, AEI, Manchester.

### A. Analyses by Gas-Liquid Chromatography (GLC) and Product Identification

A Burrell Model K-2 Kromo-Tog, equipped with an integrator, was used for all GLC analyses, utilizing the following 2.5 m columns: silicone rubber, neopentylglycol succinate, and Apiezon L, each 25% by weight on Gas-Chrom P (60-80 mesh). For complete separation of the products of metalation and alkylation it was necessary to change from one column to another. Helium, at a flow rate of about 100 ml/minute was the carrier gas. Column temperatures varied with the different packings, but were



adjusted to give maximum separation of the products. In general, temperatures of 120-175° were used for the indenenes, and 175-210° for the acenaphthene derivatives. Products were identified by comparison of their retention times with those of authentic samples, as well as by their isolation via the Kromo-Tog and subsequent analysis by NMR and IR spectral determinations. The paper areas of the various product peaks were measured by an integrator. Analysis of carefully weighed authentic mixtures of the reaction products showed that these paper areas could be used as a direct measure of molar compositions of the reaction mixtures. In the indene case, the addition of a carefully weighed amount of tert-butylbenzene as an internal standard allowed the calculation of the weights of each individual product, and hence determination of the absolute per cent recovery.

#### B. Solvents and Chemicals

1,2-Dimethoxyethane (DME), commercially available, was refluxed overnight over potassium, then distilled twice from the same metal before use (b.p., 83°/700 mm). Analysis by GLC showed it to be free from contaminants.

Potassium metal (BDH reagent), and lithium metal (Fisher Scientific Co., Lithium Corporation of America) were freed from encrusting oxide or nitride while under Skellysolve B or paraffin oil. Fisher lithium was used during the indene portion of this work, while lithium wire (1/8 inch diameter) from the Lithium Corporation was taken for the acenaphthene



reactions.

Indene (Eastman Kodak Co.), practical grade, was treated with Drierite, then distilled twice at atmospheric pressure (b.p., 176-177°/700 mm). Analysis by GLC showed it to be free from impurities and water.

Indan (practical grade) was obtained commercially from Matheson Chemical Co..

Fluorene (Eastman Kodak Co., 98%) was crystallized six times from 95% ethyl alcohol and then heated for 4 hours at 65° under vacuum in an Abderhalden drier to remove solvent. It was then dried under the same conditions but in the presence of phosphorus pentoxide. The product was stored in a desiccator over phosphorus pentoxide.

Acenaphthene (Eastman Kodak Co.) was recrystallized three times from 95% ethyl alcohol, air dried, and then dried for 8 hours at 65° under vacuum in an Abderhalden drying pistol. The pure product (m.p., 94-95°) was stored in a desiccator over phosphorus pentoxide.

C. Experimental Work Concerned with the Preparation of Methylated Indenes and Indan

Trans-3-hydroxy-1-phenyl-1-butene (LIV) was prepared according to the procedure of Braude et al (85). Freshly distilled cinnamaldehyde (122 gm, 0.925 mole) in 200 ml of ether was added to an ethereal solution of methylmagnesium iodide (from 24 gm (1.0 mole) magnesium metal and



sufficient methyl iodide) over a period of 5 hours with stirring, the reaction temperature being kept at 10-20°. The thick, grey mixture was stirred at room temperature for an additional 15 hours, and decomposed with cold, saturated ammonium chloride solution. The ether extract was dried (anhydrous  $K_2CO_3$ ), then freed from solvent. Final distillation under reduced pressure afforded 112 gm (82%) of the desired alcohol, obtained as a pale-yellow oil boiling at 100°/1.3 mm. Lit. b.p., 104°/1 mm (85).

3-Hydroxy-1-phenyl-1-butyne (LVII) was prepared following published procedures (50). To approximately 300 ml of ethereal Grignard solution, obtained from 34 gm (1.40 moles) of magnesium and 170 gm (1.56 moles) of ethyl bromide, 135 gm (1.32 moles) of ethynylbenzene was slowly added with stirring. When ethane was no longer evolved, 80 gm (1.82 moles) of acetaldehyde in 250 ml of ether was slowly added, the reaction flask being kept cold in an ice-salt bath. The reaction mixture was stirred overnight, after which the complex was decomposed with sufficient 10% sulfuric acid. The ether extract was dried ( $MgSO_4$ ) and distilled, providing 125 gm (65%) of pure, colorless product. B.p., 120°/5.0 mm. Lit. b.p., 128°/9 mm (50). The infrared spectrum (film) showed broad hydroxyl absorption between 3600 and 3100  $cm^{-1}$ , as well as the characteristic triple bond signal at 2230  $cm^{-1}$  (132). The NMR spectrum also agreed with the proposed structure.

Cis-3-hydroxy-1-phenyl-1-butene (LV)

(1) Low-pressure reduction of 0.2 mole of the substituted 1-butyne in



50 ml of anhydrous methyl alcohol with 1-2 gm of Raney nickel (144) occurred very rapidly at room temperature, 0.2 mole of hydrogen being taken up within 20 minutes. Distillation under reduced pressure gave a 90% yield of product, presumed to be cis-3-hydroxy-1-phenyl-1-butene, b.p., 99-100°/2.6 mm. Lit b.p. for the cis compound, 144°/21 mm (84). GLC analysis indicated the presence of four components, the largest being 60% of the total mixture.

(2) Hydrogenation of LVII primarily to cis-3-hydroxy-1-phenyl-1-butene could be accomplished by the use of Lindlar's catalyst (86). Fifty gm of 3-hydroxy-1-phenyl-1-butyne, 100 ml of n-heptane, 5 gm of catalyst, and 2 gm of quinoline were placed in an hydrogenation bottle and shaken with hydrogen (initial pressure, 50 p.s.i.) at room temperature till no more gas was taken up (3-4 hours). Removal of the solvent and vacuum distillation yielded an almost colorless oil (92%), of which approximately 90% was assumed to be the cis isomer, as indicated by GLC. B.p., 106-107°/4.4 mm. Lit. b.p., 144°/21 mm (84).

Cis- and trans-3-chloro-1-phenyl-1-butene could be prepared from the corresponding alcohols according to the method of Muskat and Herrman (84). Anhydrous hydrogen chloride was bubbled for approximately 2 hours through a solution of 35 gm of each of cis- and trans-3-hydroxy-1-phenyl-1-butene in 70 ml of dry ether, continually cooled at 0° in an ice-water bath. In the first attempt at isolation of the product, washing of the ethereal solution with 10% aqueous sodium hydroxide and then with water seemed to



hydrolyze some of the allylic chloride; hence excess hydrogen chloride and solvent were removed by water-pump. This resulted in the formation of two layers. The upper layer was separated, dried ( $\text{MgSO}_4$ ), and distilled under vacuum affording trans-3-chloro-1-phenyl-1-butene (19 gm, 49% yield), boiling at  $100-110^\circ/6$  mm (lit. b.p.,  $104^\circ/6$  mm(84)) and cis-3-chloro-1-phenyl-1-butene (13 gm, 34% yield), of boiling point  $96-98^\circ/3.2$  mm (lit. b.p.,  $108^\circ/6$ mm (84)).

Attempted cyclizations for the preparation of 1-methylindene

- (1) Fifty gm of trans-3-hydroxy-1-phenyl-1-butene (LIV) and 140 ml of 85% phosphoric acid were mixed and then heated, with stirring, on a steam bath for 1 hour. The mixture was diluted with 200 ml of cold water, then ether extracted. The ether extract was dried ( $\text{Na}_2\text{SO}_4$ ) and distilled. Only a high-boiling, viscous oil was collected. B.p.,  $165-185^\circ/1.5$  mm.
- (2) The above experiment was repeated using 25 gm of the carbinol (LIV), but with polyphosphoric acid (70 ml of phosphoric acid and 24 gm of phosphorus pentoxide). Heating on a steam bath was carried on for only 30 minutes. The same high-boiling product resulted.
- (3) To 15 gm (0.09 mole) of trans-3-chloro-1-phenyl-1-butene in 50 ml of Skellysolve B was added 18 gm (0.135 mole) of anhydrous aluminum chloride, and the mixture then stirred at room temperature for 30 minutes. A dark-red solid formed. The reaction mixture was warmed on the steam bath for a few minutes, then diluted with 50 ml of ice-water, resulting in the formation of a solid mass which was decomposed by heat. Ether



extraction of the product, followed by work-up described in (1) above resulted in a small yield of an unknown pale-yellow liquid (b.p., 91°/4.2 mm), along with other, high-boiling fractions.

(4) In a modification of procedure (3), 12.2 gm (0.073 mole) of cis-3-chloro-1-phenyl-1-butene in 25 ml of Skellysolve B was added dropwise to 14.6 gm (0.11 mole) of anhydrous aluminum chloride in 50 ml of Skellysolve B. After the addition was completed, stirring was continued for 30 minutes, after which time hydrogen chloride was no longer evolved. Work-up of the ether extract as in procedure (3) again failed to give the desired product as indicated by an NMR spectrum of the material obtained.

(5) Thirty-five gm of cis-3-hydroxy-1-phenyl-1-butene (LV) was added to 100 ml of phosphoric acid containing 35 gm of phosphorus pentoxide, and the mixture heated and stirred on a steam bath for 30 minutes. Steam distillation of the reaction mixture followed by distillation of the product under reduced pressure gave 3-4 ml of a colorless oil boiling at 46-47°/2.3 mm. GLC analysis indicated the presence of a number of constituents, the largest one being approximately 60% of the total. By retention time of an authentic sample, approximately 20% of the reaction mixture was shown to be 3-methylindene. Separation of the main component (60%) by GLC yielded a pure, colorless oil, the NMR spectrum of which contained all the signals expected for 1-methylindene (Fig. 1).

3-Methyl-1-indanone (LX). The preparation of 3-methyl-1-indanone could be achieved in two ways.



(1) Following the procedure of Lindenbaum (89), 120 gm (1.0 mole) of acetophenone, 200 gm (1.2 moles) of ethyl bromoacetate, and 80 gm (1.22 moles) of zinc dust were combined in 600 ml of dry benzene. After an initial warming of the mixture on a steam bath, a vigorous reaction set in. When the vigor of the reaction had diminished somewhat, the mixture was heated under reflux for 1 hour. It was then cooled, shaken with dilute sulfuric acid, the isolated benzene layer dried ( $\text{MgSO}_4$ ) and distilled. An oil was obtained boiling at 122-125°/4 mm. Lit. b.p., 146-147°/15 mm (89).

To this oil in 200 ml of benzene, 35 ml of phosphorus oxychloride ( $\text{POCl}_3$ ) was added portionwise, and the reaction mixture heated gently till reflux. (Care must be taken during the addition and heating period or else the dehydration reaction may become uncontrollable). The reaction mixture was refluxed for 45 minutes, cooled, washed twice with water to remove the inorganic substances, the organic portion then dried ( $\text{MgSO}_4$ ) and distilled under reduced pressure, yielding ethyl  $\beta$ -methylcinnamate (LVIII, 54% yield based on acetophenone). B. p., 130°/6 mm. Lit. b.p., 146-148°/16.5 mm (89).

Saponification of the ester to  $\beta$ -methylcinnamic acid was readily accomplished by refluxing for 2 hours with 300 ml of 10% aqueous sodium hydroxide. Cooling and acidification with sulfuric acid gave the acid in nearly quantitative yield. The acid was purified by recrystallization from Skellysolve B, affording white crystals melting at 94-96°. Lit. m.p.,



98.5° (153).

$\beta$ -Phenylbutyric acid was obtained in 95% yield by the room temperature reduction of  $\beta$ -methylcinnamic acid in 95% ethyl alcohol using hydrogen at 50 p.s.i. initial pressure and platinum oxide as the catalyst. After hydrogen uptake was completed, distillation furnished the carboxylic acid. B.p., 133°/1.4 mm. Lit. b.p., 168-169°/14 mm (153). The solidified acid exhibited a melting point of 35-36.5°. Lit. m.p., 47° (39-40°) (153).

$\beta$ -Phenylbutyryl chloride (LIX) was prepared in the usual manner by refluxing  $\beta$ -phenylbutyric acid with 25% excess thionyl chloride in benzene solution for 2-3 hours. Distillation under reduced pressure gave the acid chloride (97% yield), boiling at 99-100°/4.5 mm. Lit. b.p., 114°/11 mm (153).

By the Friedel-Crafts procedure (47), 60 gm (0.33 mole) of  $\beta$ -phenylbutyryl chloride in 50 ml of Skellysolve B (or CS<sub>2</sub>) was slowly added at room temperature to 65 gm (0.49 mole) of anhydrous aluminum chloride in 200 ml of Skellysolve B (or CS<sub>2</sub>) with efficient stirring. After addition of the acid chloride was completed, stirring was continued for 30 minutes, after which time 250 ml of cold water was slowly added. The ether extract was dried (MgSO<sub>4</sub>) and distilled, affording 3-methyl-1-indanone in 85% yield. B.p., 103°/3.9 mm. Lit. b.p., 132-137°/15 mm (48).

(2) The second and much simpler method for preparing 3-methyl-1-indanone employed the procedure of Koelsch et al (48). A solution of



crotonic acid (68 gm, 0.8 mole) in 500 ml of benzene was added to anhydrous aluminum chloride (318 gm, 2.4 moles), and the mixture boiled for 5 hours. Following decomposition with ice and water, the reaction mixture was extracted with ether, the ether layer washed first with sodium bicarbonate solution, then with water, and finally dried ( $\text{MgSO}_4$ ) and distilled. Ninety-four gm (82% yield) of the ketone was obtained.

3,3-Dimethyl-1-indanone (LXII) was prepared by the same procedure from 100 gm (1.0 mole) of 3-methylcrotonic acid (Aldrich Chemical Co.), 700 ml of benzene, and 400 gm (3.0 moles) of anhydrous aluminum chloride. Yield, 131 gm (82%); b.p.,  $107^\circ/4.7$  mm. Lit. b.p.,  $130-132^\circ/18$  mm (154).

3-Methylindene (XXXVIII) was prepared in 60-75% yield by the method of Parham et al (91), starting with commercially available 1-indanone (Eastman Kodak Co.). Twenty gm (0.15 mole) of 1-indanone in 150 ml of anhydrous ether was added dropwise, with stirring, to a solution of methylmagnesium iodide, prepared from 6 gm (0.25 mole) of magnesium and 40 gm (0.28 mole) of methyl iodide in the usual manner (112). After the addition was complete (approximately 60 minutes), the mixture was refluxed for 30 minutes, and then treated with 180 ml of ice and 60 ml of 20% sulfuric acid (by volume). The ether was removed from the mixture by distillation, and an additional 60 ml of 20% aqueous sulfuric acid was added. The resulting solution was refluxed for 15 minutes, and subsequently steam distilled. The organic layer was separated, dried



(MgSO<sub>4</sub>) and, after two fractional distillations, gave the product (14.8 gm) as a colorless liquid boiling at 56°/2.0 mm;  $\eta_D^{23}$ , 1.5621. Lit. b.p., 76-78°/11 mm;  $\eta_D^{25}$ , 1.5586 (91). The NMR spectrum of this compound is shown in Fig. 4.

1-Methylindene (V) was synthesized according to the scheme given by Yarboro, Karr, and Estep (39). A quantity (24 gm, 0.165 mole) of 3-methyl-1-indanone in 125 ml of ether was added dropwise to a stirred solution of 9 gm (0.24 mole) of lithium aluminum hydride in 200 ml of ether, according to general procedure (90). After 2 hours of reflux, the reaction mixture was decomposed with ice and dilute hydrochloric acid, washed with water and sodium bicarbonate solution until neutral, and dried (MgSO<sub>4</sub>). Removal of the solvent left a white solid (19.5 gm, 80% yield) recrystallizable from Skellysolve B. M.p., 70-72°; lit. m.p. for 3-methyl-1-indanol 71-72°(90).

In the absence of solvent, the alcohol was stirred and heated with 25% of its weight of solid oxalic acid, either in the anhydrous or the dihydrate form, at reflux temperature for 15-20 minutes. When the reaction mixture was cooled, the substituted indene was extracted from the solidified acid with Skellysolve B. The hydrocarbon layer was dried and fractionally distilled, giving a 40% yield of 1-methylindene as a colorless liquid boiling at 54°/3.5 mm;  $\eta_D^{25}$  1.5540. Lit. b.p., 55-56°/3.75 mm (or 186°/735 mm);  $\eta_D^{20}$  1.5565 (39). The NMR spectrum of this compound, shown in Fig. 1, corroborates the structure designated.



1,3-Dimethylindene (LXV) was prepared from the 3-methyl-1-indanone, mentioned above, by the method suggested in the literature (92). This ketone (50 gm, 0.34 mole) in 50 ml of dry ether was added dropwise to a Grignard solution obtained from 16 gm (0.66 mole) of magnesium turnings and 95 gm (0.67 mole) of methyl iodide. The mixture was refluxed for 1 hour, cooled, and worked up with cold saturated ammonium chloride solution. Separation of the organic layer and distillation of the dried ether extract under reduced pressure gave both 1,3-dimethyl-1-indanol (7.5 gm, 14% yield), m.p., 67-69°, lit. m.p., 72° (92), and 1,3-dimethylindene (colorless oil, 10 gm, 20% yield), b.p., 68°/3 mm,  $n_D^{24}$  1.5486. Lit. b.p., 66°/3 mm,  $n_D^{20}$  1.5477 (39). The NMR spectrum of 1,3-dimethylindene, shown in Fig. 5, is in agreement with the structure proposed.

1,1-Dimethylindene (LXIV) has not been reported in the literature to our knowledge. Its preparation is described below and is similar to that of 1-methylindene. Lithium aluminum hydride reduction of 3,3-dimethyl-1-indanone in a manner described earlier for 3-methyl-1-indanone afforded 3,3-dimethyl-1-indanol in 80% yield as a colorless, viscous oil boiling at 107°/4.2 mm;  $n_D^{24}$ , 1.5340. Anal. Calcd. for  $C_{11}H_{14}O$ : C, 81.44; H, 8.70. Found: C, 81.75; H, 8.66. The NMR spectrum, shown in Fig. 2, is consistent with the formulation of this compound as 3,3-dimethyl-1-indanol. The IR spectrum (film) showed broad hydroxyl absorption between 3600 and 3100  $cm^{-1}$ .



A mixture of 3,3-dimethyl-1-indanol (25 gm, 0.155 mole) and 10 gm (0.08 mole) of solid oxalic acid dihydrate was heated to reflux for 1 hour. The cooled reaction mixture was extracted with Skellysolve B to remove the oil from the solidified oxalic acid. The dried extract ( $\text{MgSO}_4$ ) was fractionally distilled through a short Vigreux column and afforded 11 gm (50% yield) of a colorless oil boiling at  $57^\circ/4.8$  mm;  $\eta_D^{23}$ , 1.5379. Anal. calcd. for  $\text{C}_{11}\text{H}_{12}$ : C, 91.61; H, 8.39. Found: C, 91.47; H, 8.20. The IR spectrum showed absorption at  $1654\text{ cm}^{-1}$  ( $\text{C}=\text{C}$ ). The NMR spectrum (Fig. 3) agreed with the proposed structure as 1,1-dimethylindene.

1,1,3-Trimethylindene (LXVI) was prepared quite readily from 3,3-dimethyl-1-indanone according to a published procedure (93). Grignard addition to 50 gm (0.31 mole) of the ketone as described for 1,3-dimethylindene gave 1,3,3-trimethyl-1-indanol, which partially eliminated water upon distillation under reduced pressure. Addition of 10 gm of oxalic acid dihydrate and a 30 minute reflux period completed the dehydration. Usual work-up by extraction and distillation as described for the preparation of 1,1-dimethylindene afforded 1,1,3-trimethylindene, 37 gm (75% yield). B.p.,  $68^\circ/3.6$  mm;  $\eta_D^{24}$ , 1.5348. Lit. b.p.,  $52-61^\circ/0.5$  mm;  $\eta_D^{25}$ , 1.5353 (93). The NMR spectrum is shown in Fig. 6.

1-Methylindan was obtained as a colorless oil by the reduction of 17 gm of 3-methylindene in 150 ml of methyl alcohol using a platinum oxide catalyst and hydrogen at an initial pressure of 50 p.s.i. The procedure



was similar to directions already published (92) for the reduction of 1,3-dimethylindene. Yield 14 gm (81%). B.p., 98°/43 mm;  $\eta_D^{24}$ , 1.5266. Lit. b.p., 189.5°/739 mm;  $\eta_D^{25}$ , 1.5241 (155°).

2,2'-Biindanyl (LXX) was prepared according to the directions of Fichter and Stenzl (99).

Eighteen gm (0.783 mole) of sodium was dissolved in 400 ml of 98% ethyl alcohol. To this solution was added 500 ml of anhydrous ether, followed by 60 gm (0.375 mole) of diethyl malonate. When the mixture had been stirred for 15-30 minutes, 100 gm (0.38 mole) of  $\alpha,\alpha'$ -dibromo-o-xylene in 700 ml of ether was added in small portions (46). After ebullition had subsided following the last of the addition, the reaction mixture was refluxed for 3 hours. Evaporation of the ether and digestion of the resulting mixture with 60 gm of potassium hydroxide in 200 ml of methyl alcohol for 30 minutes gave a blue-violet solid mass. Water (400 ml) was added and the alcohol distilled off. The cooled reaction mixture was filtered, and any remaining solids were dissolved by the addition of more water. In order to remove any organic side-products, the aqueous solution was extracted with ether. The residual aqueous layer was then acidified with concentrated hydrochloric acid, giving a light-brown precipitate, m.p., 195-196°. The reported m.p. for indan-2,2-dicarboxylic acid (XXIV) is 199°(46).

The dicarboxylic acid was heated to 200° in an oil bath till carbon dioxide evolution ceased. The dark products were dissolved in hot 5%



sodium carbonate solution, the solution filtered and acidified with concentrated hydrochloric acid. The product, after one recrystallization from water, gave 30 gm of indan-2-carboxylic acid (XXV). Yield, 49% based on dibromo xylene. M.p., 130-131°; lit. m.p., 130° (46).

Twenty gm (0.123 mole) of indan-2-carboxylic acid was mixed with 75 ml of benzene and 30 gm (0.25 mole) of thionyl chloride. The mixture was refluxed for 1.5 hours after which time the excess thionyl chloride and solvent were removed at the water-pump, and the residue distilled. Indan-2-carboxylic acid chloride, 21.8 gm (98%) was obtained as a colorless liquid, boiling at 121° /6.5 mm. Lit. b.p., 180°/100 mm (46).

Twenty gm of the acid chloride in 60 ml of chloroform was added dropwise to a mixture of 16 ml of 30% hydrogen peroxide and 37 ml of pyridine, cooled in an ice bath. The resulting peroxide precipitated, but could be brought back into solution by the addition of 50 ml of chloroform. The mixture was stirred for 15 minutes after addition was completed and, in order to remove all the pyridine and any acids, was washed twice with 33% sulfuric acid (by weight) and then with 5% aqueous sodium carbonate. The chloroform solution was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated to a small volume. Addition of Skellysolve B resulted in the precipitation of 7.5 gm (42%) of the peroxide, melting with explosive violence at 101°. Lit. decomposition point, 105° (99).

Four gm of the above peroxide was placed in a steel bomb, which was then immersed in an oil bath at 200°. The temperature dropped



rapidly to  $120^{\circ}$ , and was maintained at this point for 15 minutes by means of a bunsen flame. After the bomb was cooled and the pressure released, its brown contents was dissolved in ether, filtered, and shaken with 10% sodium hydroxide solution to remove any acidic material. When the ether solution was dried and the solvent removed, an oily solid remained. This gave a brown solid upon addition of 95% ethyl alcohol (0.6 gm, 20% yield). Three crystallizations from ethyl alcohol (Norit) gave small white needles of 2,2'-biindanyl, m.p.,  $168-170^{\circ}$ . Lit. m.p.,  $165-166^{\circ}$  (99).

Its NMR spectrum ( $\text{CDCl}_3$ ) showed a single aromatic peak at  $\tau = 2.86$ , and a broad, poorly resolved multiplet centered at  $\tau = 7.18$ . The integrated areas were in the ratio of 4:5. The infrared spectrum was also in agreement with the structure, while the mass spectrum showed a parent peak at  $m/e = 234$ .

D. General Procedure for the Formation and Collection of Hydrogen Gas

A 250 ml, round-bottom, 3-neck flask equipped with a magnetic stirrer was heated with a bunsen flame to remove adhering moisture. After it was allowed to cool (Drierite tube), it was equipped with a short water-condenser and a gas collecting apparatus. To the flask was added 100 ml of DME, 0.10 gram-atom of metal (if the metal was lithium it was cut up into small pieces) and 0.10 mole of the hydrocarbon in the order specified. But in the case of fluorene, 0.10 mole of the hydrocarbon was first dissolved in 100 ml of solvent and the metal added last. The



reaction mixture was refluxed till no more gas was evolved (from 2 to 22 hours, see Table I, p. 48). All gases were collected by the downward displacement of water. Small samples of this gas were taken and analyzed for molecular hydrogen content by mass spectrometry. Blanks were run under identical conditions except that the hydrocarbon was not added to the reaction flask.

#### Isolation of 2,2'-biindanyl from the metalation reactions

Following the general procedure for metalation described above, a mixture of 0.10 mole of indene, 0.10 mole of finely divided lithium metal (Fisher Scientific Co.) and 100 ml of DME was heated to reflux for 20 hours under an atmosphere of dry, purified nitrogen. Removal of the unreacted metal indicated that 93% of the lithium had been consumed. Decomposition of the reaction mixture with dilute hydrochloric acid, ether extraction and distillation, afforded a 76% recovery of hydrocarbon, containing 9% of indan. From the distillation residue was obtained 200-300 mg of a solid material, which melted at 171-172° after three crystallizations from ethyl alcohol. Elemental analysis and mass spectral data (parent peak at  $m/e = 234$ ) showed it to possess the formula  $C_{18}H_{18}$ . This compound was shown to be 2,2'-biindanyl by virtue of its NMR and IR spectra, which were identical in all respects with those of an authentic sample described earlier. The NMR spectrum ( $CCl_4$ ) possessed a sharp singlet at  $\tau = 2.95$  and a broad signal centered at approximately  $\tau = 7.2$ . A mixed melting point with an authentic specimen showed no depression of melting point.



Repetition of this experiment using larger pieces of lithium metal (BDH, 98%) led to only 48-50% consumption of the metal after 24 hours of reflux. Recovered by distillation was 8.7 gm (75%) of organic material, of which 23% was shown to be indan. A very small amount of the 2-indanyl dimer was also obtained. The use of potassium metal led to the formation of 17-18% of indan, and a 73% product recovery. No 2,2'-biindanyl was isolated, tarry products making up the distillation residue.

E. General Procedure for the Metalation and Methylation of the Indenes

To a dried, 3-neck 250 ml round-bottom flask, equipped with a magnetic stirrer and a reflux condenser, were added 100 ml of DME and 0.10 (or 0.20) gram-atom of metal (Li was cut into small pieces). The redistilled indene (11.6 g, 0.10 mole) was added at once to the mixture, protected by an atmosphere of purified, dry nitrogen. The mixture was refluxed for a specific length of time (see Tables II, p. 56, VII - IX, p. 86-89), then cooled in an ice-water bath. Any unreacted metal was removed mechanically as completely as possible and weighed. To the cold residual solution, now at 0-5°, was added dropwise over a period of 30-45 minutes an excess (approximately 1.5 equivalents) of methyl iodide. After the addition was completed, the reaction mixture was stirred for 30 minutes at room temperature, then decomposed with excess dilute aqueous hydrochloric acid. The mixture was then extracted twice with ether (total volume  $\approx$  400 ml), the ether extract dried ( $\text{MgSO}_4$ ), filtered and freed from solvent. The



remaining dark oil was then analyzed by GLC.

F. Analysis of Indenes on GLC Columns

The following 2.5 m columns were utilized for all GLC analyses:

Silicone rubber, 25% by weight on Gas-Chrom P (60-80 mesh). This column separated the following groups of compounds from each other but failed to separate the individuals of each group where mixtures are indicated.

(a) indan and indene, (b) 1-methylindene; 1,1-dimethylindene and 1-methylindan, (c) 3-methylindene, (d) 1,3-dimethylindene and 1,1,3-trimethylindene.

Neopentylglycol succinate, 25% by weight on Gas-Chrom P (60-80 mesh).

This column separated the following groups from each other but not the individual members of each group. (a) indan, (b) 1,1-dimethylindene and 1-methylindan, (c) indene and 1-methylindene, (d) 1,1,3-trimethylindene, (e) 3-methylindene and 1,3-dimethylindene.

Apiezon L, 25% by weight on Gas-Chrom P (60-80 mesh). This column separated the following groups from each other but not the individuals contained in each group. (a) indan and indene, (b) 1,1-dimethylindene, (c) 1-methylindene and 1-methylindan, (d) 1,1,3-trimethylindene and 3-methylindene, (e) 1,3-dimethylindene..

Use of the internal standard for the measurement of total per cent recovery

In order to determine the exact total per cent recovery in the alkylation reactions, it was found necessary to make use of an internal



standard, (S). After reaction work-up and removal of most of the solvent, a carefully weighed amount of tert-butylbenzene was introduced into the reaction flask. From the GLC chromatograms there were thus obtained the ratios of the peak area of the internal standard to that of each of the products, A, B, etc.; i.e.  $\frac{\text{Peak area of S}}{\text{Peak area of A}}$ ,  $\frac{\text{Peak area of S}}{\text{Peak area of B}}$ , etc.

By preparing and analyzing an authentic mixture of nearly the same composition as the product mixture above, the exact weight ratios  $\frac{\text{Wt. of S}}{\text{Wt. of A}}$ ,

$\frac{\text{Wt. of S}}{\text{Wt. of B}}$ , etc. and the corresponding area ratios  $\frac{\text{Peak area of S}}{\text{Peak area of A}}$ ,

$\frac{\text{Peak area of S}}{\text{Peak area of B}}$ , etc. could be calculated and measured. By making use

of the simple relationship,

$$\left[ \frac{\frac{\text{Wt. of S}}{\text{Wt. of A}}}{\frac{\text{Peak area of S}}{\text{Peak area of A}}} \right]_{\text{authentic mixture}} = \left[ \frac{\frac{\text{Wt. of S}}{\text{Wt. of A}}}{\frac{\text{Peak area of S}}{\text{Peak area of A}}} \right]_{\text{experimental product mixture}}$$

the weight of compound A, and hence its actual percentage in the experimental product mixture could be calculated, since all the other factors in the equation were known. The fact that the various products could not always be separated on one particular column obviously necessitated the above analysis to be carried out on three different columns.

## G. The Stability of the Monomethylindenes

### (1) 1 - Methylindene

#### (i) Thermal isomerization



Two gm of 1-methylindene in 10 ml of anhydrous DME was refluxed for a total of 24 hours. Periodic analyses of the mixture on a neopentylglycol succinate column revealed no change in the starting material.

Two gm of 1-methylindene was refluxed in a 10 ml pear-shaped flask. Samples were withdrawn periodically for analysis on a neopentylglycol succinate column. The results are recorded in Table III, p. 63.

(ii) Base-catalyzed isomerization

Small quantities (approximately 0.3 ml) of 1-methylindene, each in 1 ml of DME, were treated with a number of bases under varying conditions. The experimental conditions and results are listed in Table V, p. 68. The analyses were again performed on a neopentylglycol succinate column.

(iii) Acid-catalysis

A quantity of 1-methylindene (1.5 gm) in a mixture of 5 ml of DME and 3 ml of 6N hydrochloric acid was heated to reflux for 1.5 hours with efficient stirring to promote mixing of the two layers. After the reaction mixture was cooled and diluted with a small amount of ether, analysis of the orange-colored organic layer by GLC indicated no isomerization to 3-methylindene.

(2) 3-Methylindene

(i) Thermal isomerization



Five gm of 3-methylindene was refluxed in a small pear-shaped flask for up to 7 hours. Small samples were withdrawn periodically and analyzed by GLC on a silicone rubber column. The results have been recorded in Table IV, p. 65.

(ii) Isomerization in the presence of base.

Approximately 0.5 ml of 3-methylindene in 1 ml of DME was shaken with a small piece of potassium metal at room temperature for up to 5 minutes. The solution turned black in color. The unreacted metal was removed mechanically, a few drops of dilute hydrochloric acid added to the residue, and the organic layer analyzed by GLC on a silicone rubber column. No 1-methylindene was detectable, the only other product present in addition to starting material was 1-methylindan.

A repetition of the experiment, using two drops of methanolic sodium hydroxide (from 3 pellets sodium hydroxide in 10 ml of methyl alcohol) as the base and stirring at room temperature for 30 minutes also showed only 3-methylindene to be present. The use of tert-butylbenzene as an internal standard indicated that 97% of the starting material could be accounted for at the end of the reaction. Losses and polymerization are therefore virtually excluded.

H. Consumption of Excess Metal. Possible Basic Sources Leading to Polyalkylation.



Indene (11.6 gm, 0.10 mole) and potassium (7.8 gm, 0.20 mole) in 100 ml of DME were heated at reflux for 49 hours under a protective nitrogen atmosphere. From the cooled reaction mixture, 1.90 gm of metal was recovered. Thus 76% (i.e. 2.6 gm or 79% excess) of the potassium had been consumed. Decomposition with water and dilute hydrochloric acid occurred smoothly, with no violent reaction taking place and with the formation of very little hydrogen gas (~30 ml), indicating the presence of little or no free metal in the solution. Ether extraction, drying ( $\text{MgSO}_4$ ) and GLC analysis showed the product to be 17% indan and 83% indene.

In order to determine whether potassium associates with indan, 5.9 gm (0.05 mole) of indan and 1.95 gm (0.05 mole) of potassium metal in 50 ml of DME were refluxed for 46 hours under an inert nitrogen atmosphere. From the cooled solution, 1.80 gm (92-93%) of the metal could be recovered.

In order to determine whether potassium reacts or associates with potassiumindenyl, the following experiment was carried out: Indene (11.6 gm, 0.10 mole) and 3.91 gm (0.10 mole) of potassium in 100 ml of dry, purified dioxan were refluxed for 2 hours, under a nitrogen atmosphere. The cooled solution was transferred to a dry-box, and poured into 250 ml of dry pentane, where upon the black indenylpotassium salt precipitated. The solvents were decanted, the salt washed several times with dry pentane by decantation, and finally filtered by gravity. The isolated salt was



placed in a dry, clean round-bottom flask, to which 100 ml of DME and 3.91 gm of potassium were added. Removal of small quantities of pentane by distillation was followed by a 36 hour reflux period. At the end of this period, only 2.0 gm of metal could be recovered, an additional 1.9 gm having been consumed. Addition of water produced very little hydrogen gas. Indan could not be detected.

In order to determine whether potassium metal reacted with the solvent, three mixtures each containing 3.91 gm of the metal in 100 ml of DME were heated to reflux under a nitrogen atmosphere for 3, 16.5 and 36 hours. After each experiment the metal was filtered off in a dry-box, and the filtrate transferred to a second dried flask. Five gm of dry, distilled indene was added to this filtrate, and the mixture refluxed for 1 hour. To the cooled, black solution, 10-12 gm of methyl iodide was added, and the mixture stirred at room temperature for 30 minutes. Work-up as described in other alkylation reactions (p. 174) showed that the products consisted of 2% 1-methylindene and 98% indene.

After 16.5 hours of refluxing the original metal-containing solution, a small amount of sludge had formed, which was filtered off along with the unreacted metal. A considerable amount of this sludge was present after 36 hours of reflux, and was shown to be strongly alkaline to pH indicator paper. Careful decomposition of this sludge, freed of metal as much as possible, with moist ether and water and GLC analysis of the resulting mixture on a neopentylglycol succinate column (p. 175 for column details),



indicated the presence of two peaks in addition to those of ether, DME and water. The retention time of the lower-boiling component was nearly the same as that of methyl alcohol. The second unknown, having a longer retention time, was not identified, but by comparative retention times did not seem to be methyl cellosolve ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ ).

As a further experiment, a mixture of 3.91 gm of potassium in 100 ml of DME was refluxed for 17 hours, after which time the bulk of the unreacted metal was removed from the cooled solution. In addition to a number of small particles of metal remaining in the solution, the formation of some sludge was noted. Five gm of indene was added to this residual solution, the mixture refluxed for 1 hour, cooled, and alkylated with excess methyl iodide (12-15 gm). The alkylated reaction mixture was stirred at room temperature for 30 minutes and worked up as before (p.174). Analysis by GLC of the remaining oil gave the following results: 3-4% indan; 62% indene; 4% 1-methylindene; 31% 3-methylindene. From the amount of indan produced via equation (f), p. 57, about 15-20% of the methylindenes formed could be attributed to unremoved metal. Thus approximately half (15-20%) of the alkylated indene must have arisen from another source of strong base.

In a similar experiment, 0.70 gm (0.10 mole) of lithium was refluxed in 100 ml of DME for 21 hours. Removal of the metal, alkylation as described above, and GLC analysis indicated the absence of methylindenes.



I. Experimental Work Concerned with the Preparation of Methylated Acenaphthenes

1-Acenaphthenone (XLIII) was prepared according to the following two procedures:

1. Following the directions in Organic Syntheses (63), 154 gm (1 mole) of acenaphthene (95%, practical grade) and 1.1 l of glacial acetic acid were placed in a 2-l round-bottomed flask. The flask was fitted with an efficient stirrer and a thermometer extending below the surface of the liquid. The solution was stirred and heated to 60°, at which point the source of heat was removed, and 820 gm (1.2 moles) of red lead (assay 85-90%) was added in portions of about 50 gm, each portion being added as soon as the color due to the previous portion had been discharged. During this operation, which required 30-40 minutes, the temperature was maintained at 60-70° by external cooling. The reaction was complete when a portion of the solution gave no test for lead tetraacetate with moist starch-iodide paper. The dark-red syrupy solution was poured into 2 l of water contained in a large separatory funnel. The acetate was extracted first with a 350-ml portion of ether and then with a 250-ml portion of the same solvent. The combined ether extract was washed with 100 ml of water, then with 300 ml of saturated sodium chloride solution, and finally dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the solid cake washed until colorless with three 50-ml portions of dry ether. The combined filtrate and washings



were subjected to distillation. 1-Acenaphthenyl acetate distilled as a mobile, yellow oil. B.p., 155-160°/3.2 mm. Lit. b.p., 166-168°/5 mm (63). Yield: 166 gm (78%).

The acetate obtained as above was dissolved in 275 ml of methyl alcohol in a 2-l round-bottomed flask, and a solution of 40 gm (1.2 equiv.) of sodium hydroxide in 400 ml of water was added. This mixture was refluxed for 2 hours and then cooled below 20°. The yellow crystalline 1-acenaphthenol was collected on a filter and washed well with about 1.5 l of water. The crude product was air-dried (125 gm, 94%) and dissolved in nearly 2 l of boiling benzene. The solution was treated with 6-8 gm of decolorizing carbon and filtered through a heated funnel. The filtrate was concentrated to about 1 l, and the acenaphthenol allowed to crystallize. The crystals were separated by suction filtration, washed with cold benzene until the wash solvent was colorless and when dried, afforded 110 gm of 1-acenaphthenol as pale yellow-white needles, melting at 147.5-148.5°. Lit. m.p., 144.5-145.5°, and 146-148° (63).

Following the oxidation procedure of Fieser and Cason (63), a suspension of 109 gm (0.64 mole) of 1-acenaphthenol in 325 ml of glacial acetic acid was stirred mechanically and treated with a solution prepared by dissolving 47 gm (0.47 mole) of chromic anhydride in the minimum amount of water and diluting the product with 250 ml of acetic acid. The chromic acid solution was added over a period of 50-60 minutes, while a reaction temperature of 28-32° was maintained by external cooling. The



acenaphthenol dissolved with the production of a green solution and, after having been stirred for an additional hour at the same temperature, this mixture was poured into 6 liters of ice-water. The precipitated ketone was collected on a large Büchner funnel and washed well with water. Since purification by steam distillation was cumbersome, requiring approximately 40 l of distillate, the crude ketone was purified in the following manner. Fifty-gram quantities of the crude product were each dissolved in 500 ml of benzene, and the resulting solutions each shaken with 400 ml of ice-cold, 0.5N sodium hydroxide, and then 300 ml of cold, 1N hydrochloric acid. Drying ( $\text{MgSO}_4$ ) of the combined benzene layers from two such quantities and removal of the benzene solvent left 78 gm of a solid which, after two crystallizations from 95% ethyl alcohol and one recrystallization from the mixed solvent benzene-Skellysolve B (1:4), melted at  $119-121^\circ$ . Lit. m.p. for 1-acenaphthenone,  $121-121.5^\circ$  (63) and  $121-123^\circ$  (156). The final yield of pure ketone was 59 gm (55%).

2. By a method similar to that of Wenham and Whitehurst (69), 130 gm (1.09 moles) of thionyl chloride was added in portions to a solution of 100 gm (0.54 mole) of 1-naphthaleneacetic acid (Eastman Kodak Co.) in 300 ml of benzene. The mixture was stirred under reflux for 3 hours, the excess thionyl chloride and benzene removed by distillation, and the residual oil distilled under reduced pressure. A nearly quantitative yield of 1-naphthaleneacetyl chloride was obtained as a yellow oil, boiling at  $149-150^\circ/3.4$  mm. Lit. b.p.,  $188^\circ/23$  mm (153).



A solution of 59 gm (0.29 mole) of the acid chloride in 60 ml of carbon disulfide was added dropwise during approximately 30-40 minutes to a stirred suspension of 56 gm (0.42 mole) of anhydrous powdered aluminum chloride in 175 ml of carbon disulfide at room temperature. The mixture was stirred overnight (12 hours), the resulting green material then poured into ice-water, and the solid ketone along with aluminum salts separated by suction filtration. All the carbon disulfide was removed from the filtrate at the water-aspirator, and any additional ketone so obtained was collected on a Büchner funnel. Approximately 750 ml of a hot solution of benzene and Skellysolve B (1:4) was used to extract the dried solid material (53 gm), the solution filtered, and the filtrate chilled. 1-Acenaphthenone (41 gm, 84% yield) was deposited, the air-dried material melting at 119-121°. A small sample, after having been steam distilled and recrystallized from benzene-Skellysolve B (1:4) melted at 121-123°.

In an attempt to prepare 2-methyl-1-acenaphthenone (LXXVIII) from 1-acenaphthenone, by general procedures (110), a solution of 10 gm (0.06 mole) of 1-acenaphthenone, 7.1 gm (0.072 mole) of cyclohexylamine, and 100 mg of p-toluenesulfonic acid in 30 ml of benzene was warmed and refluxed for 3 hours, in an apparatus equipped with a water separator (111). During the reflux period, a yellow solid precipitated from the solution. The solution was cooled and the solid removed by filtration, washed with cold benzene, and recrystallized three times from benzene.



When dried in an Abderhalden drying pistol for 3 hours at  $75^{\circ}$  and 0.3 mm pressure, it afforded 4.5 gm of small yellow needles, melting at  $269-270^{\circ}$  (decomp., sealed tube). A halo-nujol mull showed absorptions at  $1688\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ) and  $1620\text{ cm}^{-1}$  (small shoulder,  $\text{C}\equiv\text{C}$ ), while elemental analysis indicated the absence of nitrogen in the molecule. Lit. m.p. for biacenone (LXXIX),  $262^{\circ}$  corr. (45b). Anal. Calcd. for  $\text{C}_{24}\text{H}_{14}\text{O}$ : C, 90.54; H, 4.43. Found: C, 90.42; H, 4.46.

Repetition of the above experiment without the use of p-toluene-sulfonic acid catalyst produced identical results.

Dropwise addition of the amine to a refluxing solution of the ketone in benzene solution, afforded a nearly quantitative yield of the yellow solid.

Dropwise addition of a benzene solution of the ketone to a refluxing solution of the amine in benzene resulted in the formation of a small amount of biacenone, with approximately 70% of the starting material being recovered. The presence of 200 mg of acid catalyst afforded a 40% yield of biacenone, in addition to a polymeric residue.

2-Methyl-1-acenaphthenone could be prepared from 1-naphthalene-acetic acid in the manner described for 1-acenaphthenone (p. 184). A solution of 1-naphthaleneacetic acid (400 gm, 2.15 moles) in 950 ml of 98% ethyl alcohol and 100 ml of concentrated sulfuric acid was refluxed for 2 hours. The cooled mixture was poured into 1 l of water, and extracted twice with ether. The ether layer was washed with 5% sodium bicarbonate solution until no more starting material could be recovered upon acidification



of the alkaline extracts. The ethereal solution was dried ( $\text{MgSO}_4$ ) and subsequently distilled under vacuum. Ethyl 1-naphthaleneacetate was obtained as a clear liquid, boiling at  $139-141^\circ/2.1$  mm. Lit. b.p.,  $134-141^\circ/0.8$  mm (113). The yield was 428 gm (98%, allowing for 20 gm of recovered starting material).

Although Julia (113) previously had methylated the above ester using potassium tert-butoxide as the base, in our hands the use of sodium hydride (157) was found to give better results.

In a flame-dried, 3-neck flask, fitted with a magnetic stirrer, condenser, and thermometer for measuring the internal temperature, were placed 130 gm (0.61 mole) of the ester, 800 ml of dry benzene, and 140 gm (1 mole) of methyl iodide. An Erlenmeyer flask, attached to one neck of the reaction vessel by means of a short piece of wide Tygon tubing, contained 46 gm (1 mole) of a 52% sodium hydride dispersion in paraffin oil (Metal Hydrides Inc.). The hydride was added to the reaction mixture in small portions during 1.5 hours, the temperature being maintained at  $20-25^\circ$  by external cooling. After the addition was completed, stirring was continued for 1.5 hours at room temperature, followed by an 18-hour reflux period. The reaction mixture was cooled, carefully decomposed with 200 ml of glacial acetic acid and then with 500 ml of water, and then extracted twice with ether. This benzene-ether extract was washed with water and bicarbonate solution until free from acetic acid, dried ( $\text{MgSO}_4$ ) and distilled. The yield of ethyl  $\alpha$ -(1-naphthyl)propionate was 130 gm (94%),



isolated as a clear, slightly colored liquid. B. p., 136-138°/1.8 mm.

Lit. b.p., 144-148°/0.8 mm (113).

A solution of ethyl  $\alpha$ -(1-naphthyl)propionate (430 gm, 1.89 moles) and 100 gm (2.5 moles) of sodium hydroxide in 750 ml of water was refluxed for 4 hours. The clear homogeneous solution was cooled, extracted with ether to remove unreacted ester, and the aqueous portion acidified with hydrochloric acid. The nearly white solid was collected by suction filtration, and recrystallized from aqueous ethyl alcohol. The resulting white crystals of  $\alpha$ -(1-naphthyl)propionic acid (334 gm, 91% yield) melted at 152-153°. Lit. m.p., 148-149° (158).

A solution of the naphthylpropionic acid (163 gm) and 150 gm of thionyl chloride in 450 ml of benzene was refluxed for 3 hours. The solvent and excess thionyl chloride were removed, and the  $\alpha$ -(1-naphthyl)propionyl chloride used directly for the following cyclization step.

The acid chloride (approximately 350 gm, 1.6 moles), obtained from two batches of 163 gm of  $\alpha$ -(1-naphthyl)propionic acid above, was dissolved in 300 ml of carbon disulfide, and the resulting solution added dropwise at room temperature over a period of 2 hours to a well-stirred mixture of 325 gm (2.4 moles) of granular aluminum chloride (BDH) in 1 l of carbon disulfide. The mixture, which turned dark-green and then black, was stirred overnight, and then decomposed with ice and water. The resulting dark and sticky organic fraction could not be successfully distilled under reduced pressure, and therefore was steam distilled. A



yellow oil distilled over very slowly (approximately 5 gm per 3 l of distillate). An ether extract of this oil was dried ( $\text{MgSO}_4$ ) and distilled, affording 2-methyl-1-acenaphthenone as a nearly colorless oil (137.5 gm, 47% yield), boiling at  $152-153^\circ/4.3$  mm,  $n_D^{25}$ , 1.6385. (The main cause of the low yield and the difficult work-up is believed to be due to the coarse, granular aluminum chloride used. Pure, powdered reagent should afford much better results).

When chilled, the oil solidified and, after one crystallization from a little ethyl alcohol followed by two recrystallizations from a mixture of benzene and Skellysolve B (1:4), colorless crystals were obtained. M.p.,  $33-34^\circ$ . Anal. Calcd. for  $\text{C}_{13}\text{H}_{10}\text{O}$ : C, 85.69; H, 5.53. Found: C, 85.82; H, 5.60.

The infrared spectrum ( $\text{CCl}_4$ ) showed carbonyl absorption at  $1715\text{ cm}^{-1}$ , while in the NMR spectrum ( $\text{CCl}_4$ ) a quartet at  $\tau=6.45$  ( $J=7.5$  cps) and a doublet at  $\tau=8.51$  ( $J=7.5$  cps) were present (area ratio of 1:3), in addition to six aromatic protons.

2-Methyl-1-acenaphthenone oxime, m.p.,  $126-140^\circ$ . Anal. Calcd. for  $\text{C}_{13}\text{H}_{11}\text{NO}$ : C, 79.16; H, 5.62; N, 7.10. Found: C, 79.17; H, 5.92; N, 7.25. The NMR spectrum (Fig. 7) showed it to be a nearly 50:50 mixture of isomers: hydroxyl-doublets at  $\tau=1.42$  ( $J=1$  cps),  $1.52$  ( $J=1$  cps); overlapping methynyl-quartets centered at  $5.6\tau$  ( $J=7$  cps); two overlapping methyl-doublets at  $8.32\tau$  ( $J=7$  cps). The IR spectrum ( $\text{CCl}_4$ ) showed free and bonded hydroxyl absorption ( $3600$  and  $3265\text{ cm}^{-1}$  respectively),



and C≡N absorption at  $1620\text{ cm}^{-1}$ .

2,2-Dimethyl-1-acenaphthenone (LXXX) was prepared by the exhaustive methylation of 1-acenaphthenone, following the alkylation procedure for ethyl  $\alpha$ -(1-naphthyl)propionate, described on p. 187.

Fifty gm (0.3 mole) of 1-acenaphthenone in a mixture of 400 ml of dry benzene and 110 gm (0.75 mole) of methyl iodide, was treated with 44 gm (0.91 mole) of sodium hydride dispersion (49%) at  $20-25^{\circ}$  during 2 hours. The mixture was stirred at room temperature for 1.5 hours, and at reflux temperature for another 2 hours. Decomposition and work-up as described earlier (p. 187), followed by distillation under reduced pressure gave a dark-yellow oil, boiling at  $106-106.5^{\circ}/0.6\text{ mm}$ . The oil was remethylated with 30 gm of methyl iodide and 10 gm of hydride dispersion in 250 ml of benzene as before. After work-up and complete removal of the benzene and ether solvents, the oil solidified and was crystallized from 95% ethyl alcohol, affording 48 gm (82%) of the dimethyl ketone. An analytical sample was prepared following steam distillation and four recrystallizations from ethyl alcohol. Small, colorless plates were obtained, m.p.,  $72-73^{\circ}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{O}$ : C, 85.68; H, 6.17. Found: C, 85.52; H, 6.09.

The NMR spectrum ( $\text{CDCl}_3$ ) exhibited aromatic protons and a sharp singlet ( $\tau=8.55$ ) in the ratio 1:1. A strong band at  $1718\text{ cm}^{-1}$  in the infrared ( $\text{CCl}_4$ ) indicated the presence of a carbonyl group.

The ketone was further characterized as its oxime, 2,2-dimethyl-



1-acenaphthenone oxime, m.p., 130-141°. Anal. Calcd. for  $C_{14}H_{13}NO$ : C, 79.59; H, 6.20; N, 6.63. Found: C, 79.15; H, 6.20; N, 6.33.

The NMR spectrum (Fig. 8) showed hydroxyl-doublets at  $\tau=1.38$  ( $J=1$  cps), 1.50 ( $J=1$  cps), and two methyl-singlets at  $\tau=8.15$  and 8.37 in a 16:84 ratio respectively, indicating the presence of two oximo isomers. The infrared spectrum ( $CCl_4$ ) possessed absorptions at 3595, 3270 (free and bonded hydroxyl), and  $1618\text{ cm}^{-1}$  ( $C=N$ ).

1-Methylacenaphthene (LXXXII) was prepared by either of the following two methods.

(1) Following the procedure used by Brown and Hammick (114) as well as by Lozac'h and Mollier (159), a solution of 50 gm (0.3 mole) of 1-acenaphthenone in 600 ml of benzene was added dropwise, during 2-2.5 hours, to a Grignard reagent prepared from magnesium (11 gm, 0.45 mole) and methyl iodide (75 gm, 0.53 mole) in 200 ml of ether. The reaction mixture was stirred at room temperature for 1 hour, and decomposed with ice and saturated ammonium chloride solution, as well as with dilute hydrochloric acid. The organic layer was washed with water, dried ( $MgSO_4$ ) and concentrated to a small volume. To this residual oil, 500 ml of ethyl alcohol was added, of which 200 ml was removed by distillation in order to eliminate all of the benzene. On addition of a solution of 75 gm of picric acid in 1600 ml of ethyl alcohol the picrate of 1-methylacenaphthylene separated as a mass of orange-red needles. Recrystallization from alcohol gave 65 gm of orange-red needles, melting at 187-188°. Lit. m.p., 178-



179° (114). Decomposition of the picrate with excess sodium hydroxide in a large volume of water and extraction with ether, yielded the known 1-methylenacenaphthylene as a dark-orange liquid (27 gm, 55%). In the NMR ( $\text{CDCl}_3$ ), a vinyl proton at 3.42 $\tau$  ( $J=1.5$  cps) and a methyl signal at 7.75 $\tau$  ( $J=1.5$  cps) appeared.

Reduction of this aromatic olefin at room temperature in 150 ml of ethyl alcohol with platinum oxide and hydrogen at 50 p.s.i. occurred readily, producing a colorless oil (85% yield) which yellowed on standing. GLC indicated a 95-96% purity. B.p., 92-94°/0.9 mm. Lit. b.p., 145-155°/28 mm (114).

(2) By means of a Wolff-Kishner reaction, following the procedure of Anderson and Wade (55), a mixture of 20 gm (0.11 mole) of 2-methyl-1-acenaphthenone in 70 ml of 95% ethyl alcohol and 100 ml of 85% hydrazine hydrate was refluxed for 1.5 hours. To this was added 100 ml of diethylene glycol, and ethyl alcohol, water, and excess hydrazine were removed by distillation till a temperature of 160-165° was reached. After addition of 14 gm (0.25 mole) of potassium hydroxide, followed by a further reflux period of 4 hours, 100 ml of water was added to the cooled solution. The three successive ether extracts were combined and washed with water, dried, and distilled, giving 13 gm (70%) of pure 1-methylenacenaphthene, boiling at 94°/1.2mm.  $\eta_D^{24}$ , 1.6180. The NMR spectrum of this compound is shown in Fig. 9.

1,1-Dimethylenacenaphthene (XCIII) was obtained in 50% yield by a



Wolff-Kishner reduction similar to the reaction described above for 1-methylacenaphthene. From 25 gm (0.128 mole) of 2,2-dimethyl-1-acenaphthenone and 125 ml of 85% hydrazine hydrate in 90 ml of ethyl alcohol, along with 125 ml of diethyleneglycol and 16.5 gm (0.295 mole) of potassium hydroxide added at the appropriate time, 11.5 gm of 1,1-dimethylacenaphthene was obtained as a clear yellow liquid, boiling at 97-98°/1.5 mm;  $n_D^{23}$ , 1.6001. Anal. Calcd. for  $C_{14}H_{14}$ : C, 92.26; H, 7.74. Found: C, 92.51; H, 7.44.

Its NMR spectrum (neat) possessed two singlets at  $\tau=7.11$  ( $CH_2$ ) and 8.85 ( $CH_3$ ) in the area ratio of 1:3.

The picrate was obtained as orange needles from a small amount of 95% ethyl alcohol. M.p., 112-112.5°. Anal. Calcd. for  $C_{20}H_{17}N_3O_7$ : C, 58.39; H, 4.17; N, 10.21. Found: C, 58.41; H, 4.44; N, 10.11. The picrate decomposed readily in solvents such as ether and hexane, and even on drying at 75°/2 mm.

A mixture of cis- and trans-1,2-dimethyl-1-acenaphthenol was obtained by the reaction between 2-methyl-1-acenaphthenone (25 gm, 0.138 mole) in 250 ml of benzene and methyl Grignard (from 5.1 gm, 0.21 mole of magnesium and 45 gm of methyl iodide in 200 ml of ether). Following addition of the ketone, the mixture was refluxed for 2 hours, cooled, and decomposed with ice and saturated ammonium chloride solution. The aqueous layer was extracted (ether), the ether-benzene solution thus obtained was dried ( $MgSO_4$ ), and the solvent evaporated. A 93% yield (25.4 gm) of a pale-yellow solid was obtained, which, after one recrystal-



lization from ethyl alcohol (Norit) and three recrystallizations from Skelly-solve B, gave colorless crystals turning slightly yellow on standing at room temperature. The broad melting point range ( $88-101^{\circ}$ ) indicated a mixture of isomers. This was supported by the NMR spectrum (Fig. 10) which showed two different methyl signals at  $\tau=8.38$  and  $8.58$  in addition to an expected methyl-doublet. Resolution on an A-60 instrument was inadequate, but use of a high resolution instrument (HR-100) led to clear separation of all signals. Peak identification was achieved by use of coupling values and side-band irradiation, which caused collapse of the methyl-doublet into a single peak. Integration values indicated a 54:46 ratio of isomers. Anal. Calcd. for  $C_{14}H_{14}O$ : C, 84.81; H, 7.12. Found: C, 84.46; H, 6.87.

A quantity (20.7 gm, 0.105 mole) of cis- and trans-1,2-dimethyl-1-acenaphthenol was dissolved in a minimum amount of hot 95% ethyl alcohol, and this was added immediately to a hot solution of 24 gm (0.105 mole) of picric acid in 250 ml of ethyl alcohol. The picrate of 1,2-dimethylacenaphthylene precipitated immediately from the hot solution, and was collected and recrystallized three times from ethyl alcohol, affording orange needles, (41 gm, 92%) melting at  $194-195^{\circ}$  (decomp.). Anal. Calcd. for  $C_{20}H_{15}N_3O_7$ : C, 58.68; H, 3.69; N, 10.27. Found: C, 58.63; H, 3.85; N, 10.38.

Decomposition of 40 gm of the picrate with excess sodium hydroxide in large quantities of water (necessary to dissolve all of the sodium picrate),



was followed by ether extraction of the resulting yellow solid. The ether extract was thoroughly washed with water, dried ( $\text{MgSO}_4$ ) and freed from solvent, thus affording 1,2-dimethylacenaphthylene (LXXXIII) in 97% yield. Yellow plates, obtained after three recrystallizations from ethyl alcohol, melted at  $71.5-72^\circ$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{12}$ : C, 93.29; H, 6.71. Found: C, 93.48; H, 6.65.

The infrared spectrum ( $\text{CCl}_4$ ) showed unsaturation at  $1620\text{ cm}^{-1}$ , while the NMR spectrum ( $\text{CDCl}_3$ ) possessed a single peak ( $\tau = 7.85$ ) for the two methyl groups in addition to the aromatic protons at  $2.3-2.75\tau$ .

Diimide reduction of 1,2-dimethylacenaphthylene according to published procedures (115, 160) was attempted as follows.

A mixture of 5 gm of the olefin in 65 ml of methyl alcohol, 6.5 gm of 85% hydrazine hydrate, and a small amount of cupric sulfate was stirred at  $45-50^\circ$  for 1 week, with air being bubbled through the solution. Small quantities of hydrazine hydrate along with fresh catalyst were added every 12 hours. As well, methyl alcohol was added to offset losses due to evaporation. The reaction mixture was filtered, the solvent removed, and the residue taken up in ether. The ether fraction was washed with dilute hydrochloric acid, concentrated, and analyzed by GLC. Starting material, to the extent of 43% was still present, along with 13% of an unknown higher-boiling impurity.

Cis-1,2-dimethylacenaphthene (LXXXIV) was prepared by the room temperature reduction of 5 gm of 1,2-dimethylacenaphthylene in 100 ml of



ethyl alcohol, using platinum oxide as the catalyst and hydrogen at an initial pressure of 20 p.s.i. When hydrogen take-up was complete, the solution was filtered, and the solvent removed, leaving a grey solid of 96% purity in quantitative yield. Three recrystallizations from alcohol (Norit) yielded beautiful, colorless needles, m.p., 53-54°. Anal. Calcd. for  $C_{14}H_{14}$ : C, 92.26; H, 7.74. Found: C, 92.38; H, 7.63.

The NMR spectrum of this compound is shown in Fig. 11 and agrees with the structure as 1,2-dimethylacenaphthene.

Its picrate (from alcohol) possessed fine orange needles, m.p., 116-117°. Anal. Calcd. for  $C_{20}H_{17}N_3O_7$ : C, 58.39; H, 4.17; N, 10.21. Found: C, 58.27; H, 4.27; N, 10.41.

Attempted reactions for the preparation of trans-1,2-dimethyl-acenaphthene

Using a Reformatsky reaction (89), 2 gm of zinc dust (previously washed with 2% HCl, water, ethyl alcohol, acetone, ether, and then dried at 110°), 5 gm of 2-methyl-1-acenaphthenone, and 5.5 gm of ethyl bromoacetate were mixed in 20 ml of benzene and the resulting mixture refluxed for 2-3 hours. The cooled mixture was taken up in ether, the ether solution was washed with 20% sulfuric acid, dried, and then freed from solvent. The resulting oil was treated with 3 ml of phosphorus oxychloride in 20 ml of benzene, the solution refluxed for 1 hour, cooled, and washed twice with water. The dark oil which was obtained upon removing the solvents was saponified for 3 hours with excess aqueous sodium hydroxide. Acidification



gave 6.3 gm of a crude solid. A solution of this solid in a hot mixture of 500 ml of water and 200 ml of ethyl alcohol was filtered, and when cooled, deposited 3.8 gm (61%) of a carboxylic acid, shown by NMR to be 2-methyl-1-acenaphthyleneacetic acid (LXXXVII). M.p., 154-156°. The NMR spectrum (CDCl<sub>3</sub>) showed peaks at  $\tau = -0.50$  (broad singlet), 6.29 (singlet), and 7.69 (singlet) in the area ratios of 1:2:3. An analytical sample of this compound was not prepared.

The preparation of glycidic esters according to the procedures of Darzens and Delépine (118) was found to be unsuccessful. From the reactions between 2-methyl-1-acenaphthenone, ethyl dichloroacetate and magnesium amalgam, or ethyl dibromoacetate and zinc dust, nearly all the starting material could be recovered.

A mixture of cis- and trans-2-methyl-1-acenaphthenol (LXXXVIII) was obtained by the lithium aluminum hydride (1.5 gm, 0.04 mole in 20 ml of ether) reduction of 5 gm (0.0275 mole) of 2-methyl-1-acenaphthenone in 15 ml of ether (90). Isolation of the product by acid decomposition, ether extraction, washing of the ether extract with water, drying (MgSO<sub>4</sub>) and solvent removal gave a quantitative yield of a white solid. One crystallization from Skellysolve B gave a melting point of 73-85°. The ratio of trans/cis isomers was found to be 55:45 by the interpretation of the NMR spectrum (CDCl<sub>3</sub>), the two doublets at  $\tau = 4.60$  ( $J = 6.5$  cps) and 4.98 ( $J = 2$  cps) being assigned to the cis and trans isomers respectively. The complete spectrum is shown in Fig. 12.



To a cold ethereal solution (50 ml) of 5 gm (0.027 mole) of the cis and trans carbinol, 2.7 gm (0.01 mole) of phosphorus tribromide was added, and the solution stirred at 0-5° for 30 minutes (122). The solution was then washed successively with water, aqueous sodium bicarbonate, and then water. The dried (MgSO<sub>4</sub>) solution freed from solvent left a mixture of cis- and trans-2-methyl-1-bromoacenaphthene as an oil. The NMR spectrum (Fig. 13) again proved it to be a mixture, the C<sub>1</sub>-proton of the cis isomer occurring at 4.18  $\tau$  (J=7 cps), that of the trans bromide at  $\tau$ =4.77 (J=3 cps). Integration values gave a 62:38 trans/cis ratio.

The bromide lost hydrogen bromide very readily, even during solvent removal. On distillation, under reduced pressure, polymerization occurred with loss of hydrogen bromide.

Following the procedure of Adams and Thal (123), the above bromide in ethyl alcohol was added slowly to a solution of 2.2 gm (0.034 mole) of potassium cyanide in 10 ml of water, and the mixture refluxed for 4 hours, during which time it blackened. The bulk of the alcohol was removed and the organic material extracted from the aqueous layer with ether. From the ether extract a dark residual oil was obtained, from which none of the expected carboxylic acid could be isolated upon treatment with excess potassium hydroxide (161).

Following published directions for the preparation of 1-acenaphthenyl methyl ether (124), a solution of the above bromide (5 gm) in 25 ml of methyl alcohol was refluxed for 4-5 hours, then cooled, treated with ether



and washed with bicarbonate solution and water. Removal of the solvent from the dried solution yielded a mixture containing 80-85% of 1-methyl-acenaphthylene and 15-20% of the expected 2-methyl-1-acenaphthenyl methyl ether (cis and trans) as determined by GLC and NMR.

Repeating the work of Maxim (125), solid acenaphthenequinone was added to a methyl Grignard solution in a manner described earlier (p. 191 ). A black solid was obtained as the product, which did not give the desired diolefin upon acid treatment.

The condensation of 1-acenaphthenone with formaldehyde (37%) in an aqueous solution in the presence of sodium hydroxide did not produce any of the 2-hydroxymethyl-1-acenaphthenone (m.p., 213-215°) as reported by Gault and Kalopissis (124).

Reaction between cis-1,2-dimethylacenaphthene and n-butyllithium

A mixture of 1.5 gm (0.00825 mole) of cis-1,2-dimethylacenaphthene and 8 gm (0.019 mole) of n-butyllithium solution (15% in hexane, Foote Mineral Co.) was refluxed for 21 hours. All gases evolved were collected by the downward displacement of water. Of the 75-80 ml of gas collected, a small sample was analyzed on a mass spectrometer, and was found to contain no trace of n-butane. The reaction mixture, which originally was colorless but later changed to dark-green and then black, was cooled, decomposed with dilute hydrochloric acid, and then extracted with ether. From the ether extract there was obtained a brown solid which was shown to be the original starting material after one crystallization from alcohol



(90% recovery, m.p., 53-54°).

A similar reaction between 2 gm (0.013 mole) of acenaphthene and 10 gm (0.023 mole) of 15% n-butyllithium in hexane refluxed for 23 hours evolved 85-90 ml of gas, which contained a small amount (1-2%) of n-butane. To the cooled solution, 25 gm (0.175 mole) of methyl iodide was added, and the mixture then stirred and warmed for 1 hour. Addition of dilute hydrochloric acid, ether extraction, drying of the ether extract ( $\text{MgSO}_4$ ) and removal of the ether gave starting material and none of the methylated acenaphthene whatsoever.

The experiment was repeated with the exception that 15 ml of DME was used as an additional solvent, and that n-butyllithium from a freshly-opened bottle was used. Even though addition of the base caused an instantaneous black coloration, no methylacenaphthenes were found after treatment of the black solution with methyl iodide.

Acenaphthene (3 gm, 0.0195 mole) was added to a solution of sodium methylsulfinyl carbanion (prepared from 2 gm of sodium hydride (56% dispersion) and 20 ml of DMSO (130)), and the resulting black solution stirred at 60-65° for 15 hours. The reaction mixture was cooled, 25 gm of methyl iodide was added (exothermic reaction), and the resulting mixture was stirred at room temperature for 15 minutes. After the reaction mixture was acidified, extracted with chloroform, the chloroform extract washed three times with water, the dried organic layer was concentrated to a dark oil which contained mostly starting material and no methylated



acenaphthene whatsoever.

1,2,2-Trimethyl-1-acenaphthenol (XCIV) was prepared by the dropwise addition of 10 gm (0.051 mole) of 2,2-dimethyl-1-acenaphthenone in 100 ml of benzene to a Grignard solution made from 2 gm (0.082 mole) of magnesium and 15 gm (0.105 mole) of methyl iodide in 80 ml of anhydrous ether. The mixture was refluxed for 1 hour, and subsequently decomposed with ice and saturated ammonium chloride solution. The organic portion was washed with water, dried ( $\text{MgSO}_4$ ) and evaporated to dryness, affording a quantitative yield of crude 1,2,2-trimethyl-1-acenaphthenol as a pale-yellow solid. Three recrystallizations from 95% ethyl alcohol (Norit) yielded small colorless crystals, melting at 101-102°. The carbinol decomposed slowly on standing. Anal. Calcd. for  $\text{C}_{15}\text{H}_{16}\text{O}$ : C, 84.86; H, 7.60. Found: C, 84.89; H, 7.40.

The NMR spectrum (Fig. 14) showed a single hydroxyl peak at 8.0  $\tau$ , and three different methyl groups at  $\tau=8.49$ , 8.67, and 8.74. In the infrared ( $\text{CCl}_4$ ), a sharp absorption at  $3620\text{ cm}^{-1}$  (free OH) occurred, with little hydrogen bonding indicated.

The carbinol (50 gm, 0.236 mole) was dehydrated with a slight excess of picric acid, as described on p. 194. Decomposition of the picrate with base, ether extraction and distillation of the dried ether solution under vacuum afforded 41.5 gm (91%) of 2,2-dimethyl-1-methylene-acenaphthene (XCV) as a pale-yellow oil, b.p., 101.5-102°/0.9 mm.

$\eta_D^{22}$ , 1.6315. Anal. Calcd. for  $\text{C}_{15}\text{H}_{14}$ : C, 92.74; H, 7.26. Found:



C, 92.61; H, 7.26.

The NMR spectrum (Fig. 15) corroborates the structure of the exocyclic olefin.

The orange picrate, obtained from ethyl alcohol by freezing in a refrigerator, melted initially at 62-63° (decomp.), with further decomposition at 85-100°. Anal. Calcd. for  $C_{21}H_{17}N_3O_7$ : C, 59.57; H, 4.05; N, 9.93. Found: C, 59.22; H, 4.21; N, 10.13.

At room temperature, hydrogen bromide was bubbled through a neat solution of the exocyclic olefin until the equivalent amount of gas had been added to the double bond. The solution was taken up in ether, washed with water, dried, and distilled under reduced pressure. Only starting material was recovered in quantitative yield.

1,1,2-Trimethylacenaphthene (XCVI) was prepared by three routes.

(1) The first method involved a catalytic reduction of 2,2-dimethyl-1-methyleneacenaphthene, by the method described for 1-methylacenaphthene (p. 192) and for cis-1,2-dimethylacenaphthene (p.195). The yield of the colorless product after distillation was 90%, b.p., 98-99°/1.0 mm. A 5% impurity was present, but this could be removed by GLC purification on a 20-ft. preparative column of butanediol succinate, 20%, on Gas-Chrom W, at 200° C. The pure 1,1,2-trimethylacenaphthene (NMR spectrum Fig. 17) boiled at 108°/1.5 mm;  $\eta_D^{25}$ , 1.5932. Anal. Calcd. for  $C_{15}H_{16}$ : C, 91.78; H, 8.22. Found: C, 91.65; H, 7.98.

Picrate: pale-orange needles, from alcohol. Initial decomp.



point 71-72°, with further decomp. up to 105°. Anal. Calcd. for  $C_{21}H_{19}N_3O_7$ : C, 59.29; H, 4.50; N, 9.88. Found: C, 59.28; H, 4.72; N, 9.86.

(2) By the second method, 5 gm of 2,2-dimethyl-1-methyleneacenaphthene in 40 ml of THF was refluxed with 2 gm of lithium aluminum hydride (two-fold excess) for 20 hours. Work-up as described elsewhere (p. 197) and chromatography on neutral alumina with Skellysolve B as eluant gave a nearly colorless liquid (4 gm), better than 98% pure (by GLC), and shown to be the trimethylacenaphthene by its NMR spectrum (Fig. 17).

(3) A third method for preparing 1,1,2-trimethylacenaphthene was by the reduction of 2,2-dimethyl-1-hydroxymethylacenaphthene p-toluenesulfonate, a compound obtained from 2,2-dimethyl-1-hydroxymethylacenaphthene, whose preparation is described immediately following this description of the reduction.

To 1 gm (0.026 mole) of lithium aluminum hydride in 50 ml of ether, an ethereal solution of 4.4 gm (0.012 mole) of 2,2-dimethyl-1-hydroxymethylacenaphthene p-toluenesulfonate was added dropwise over 1 hour (162). The reaction mixture was stirred at room temperature for 1 hour, and then refluxed for 16 hours. Decomposition with ethyl acetate and water was followed by ether extraction. The ether extract was filtered and dried ( $MgSO_4$ ). Solvent removal left 2.4 gm of a pale-yellow oil, which was chromatographed on neutral alumina with Skellysolve B as the eluant. A colorless oil was obtained (2.3 gm, 97% yield), which



was shown to be 1,1,2-trimethylacenaphthene by its NMR spectrum (Fig. 17).

2,2-Dimethyl-1-hydroxymethylacenaphthene (XCVII) was prepared by the hydroboration reaction on 2,2-dimethyl-1-methyleneacenaphthene according to the procedure of H. C. Brown (127). In a 1000-ml, 3-neck flask, equipped with a magnetic stirrer, dropping funnel, condenser, and a nitrogen inlet, were placed 110 ml of a 1.0 M solution of sodium borohydride in diglyme, and 50 gm (0.258 mole) of 2,2-dimethyl-1-methyleneacenaphthene in 30 ml of diglyme. The flask was immersed in a water bath (approx. 20°) and flushed with nitrogen, and subsequently a static nitrogen atmosphere was maintained. From a dropping funnel, 18 ml of freshly-distilled boron trifluoride etherate was added dropwise, the reaction temperature being maintained at 20-25°. Stirring at this temperature was continued for 1 hour, and the excess hydride destroyed by the careful, dropwise addition of 30 ml of water. The organo borinic acid was oxidized at 40-50° by addition first of 28 ml of 3N sodium hydroxide, followed by a short period of stirring at this temperature, and then dropwise addition of 28 ml of 30% hydrogen peroxide. The mixture was stirred at room temperature for 1 hour, extracted with ether, and the ether layer washed five times with cold water to remove all the diglyme. Drying of the ether solution ( $\text{MgSO}_4$ ) and removal of the solvent left 53 gm (97%) of a pale-yellow, viscous oil. Distillation under reduced pressure of a small amount of the product, using steam to heat the condenser, gave 2,2-dimethyl-



-1-hydroxymethylacenaphthene as an extremely viscous, nearly colorless oil, of 97-98% purity as shown by GLC analysis. B.p., 140-141°/0.75 mm;  $\eta_D^{24.5}$ , 1.6149. Anal. Calcd. for  $C_{15}H_{16}O$ : C, 84.86; H, 7.60. Found: C, 84.55; H, 7.60. The NMR spectrum of this compound is shown in Fig. 16, and agrees completely with the assigned structure.

The 3,5-dinitrobenzoate derivative was a yellow solid (from chloroform), m.p., 200-201°. Anal. Calcd. for  $C_{22}H_{18}N_2O_6$ : C, 65.02; H, 4.46; N, 6.90. Found: C, 65.25; H, 4.61; N, 6.66.

2,2-Dimethyl-1-hydroxymethylacenaphthene p-toluenesulfonate was prepared by adding a solution of p-toluenesulfonyl chloride (10 gm, 0.053 mole) in 30 ml of pyridine to 8 gm (0.038 mole) of 2,2-dimethyl-1-hydroxymethylacenaphthene in 30 ml of pyridine. The mixture was kept at room temperature for 2 days and then poured into 400 ml of ice-water, and extracted twice with chloroform. The combined chloroform extracts were washed three times with 200 ml of cold, 6N hydrochloric acid, two times with 200 ml of cold, saturated sodium bicarbonate solution, and twice with water. When dried ( $CaCl_2$ ) and freed from solvent, 13.3 gm of crude p-toluenesulfonate remained as a thick, yellow oil. This oil was dissolved in excess, hot 98% ethyl alcohol, and when cooled deposited 9.8 gm (70%) of grey crystals. Two recrystallizations from ethyl alcohol gave white crystals, m.p., 72-73°. Anal. Calcd. for  $C_{22}H_{22}O_3S$ : C, 72.10; H, 6.05; S, 8.75. Found: C, 71.94; H, 6.06; S, 9.00.

2,2-Dimethyl-1-acenaphthenecarboxaldehyde (XCIX) was obtained



by oxidation of 2,2-dimethyl-1-hydroxymethylacenaphthene according to the procedure of Barton et al (129).

Phosgene was bubbled into a stirred solution of 400 ml of dry ether for 1 hour. To this solution was added 50 gm (0.236 mole) of the primary alcohol in 100 ml of ether. Stirring was continued at room temperature for 2 hours, while phosgene was continually passed into the solution. This procedure was repeated until, after evaporation of the solvent, the infrared spectrum of a sample of the product was free from hydroxyl absorption. In this manner, 63 gm (97%) of the chloroformate was obtained as a viscous, pale-yellow oil, boiling at 150-151°/0.8 mm. This formate ester darkened to a black color on standing at room temperature for a prolonged period of time.

After evaporation of the solvent, the crude chloroformate ester was put into a 1000-ml flask, treated with 300 ml of DMSO (dried by passage through a column of molecular sieves and distilled under reduced pressure from calcium hydride), and the whole mixture then stirred at 15° for a few minutes. A vigorous evolution of carbon dioxide took place. After evolution of carbon dioxide had ceased, the solution was stirred at room temperature for 15-20 minutes, whereupon 120 ml of dry, distilled triethylamine was added in a dropwise fashion during a 20-to 30-minute period, while the reaction was kept cool in an ice-water bath. Cooling caused some of the DMSO to solidify, but this was corrected by warming the reaction vessel slightly after addition of the amine was completed.



The mixture was then stirred at room temperature for 1 hour, after which time 200 ml of water, and a sufficient amount of 2 N hydrochloric acid to acidify the solution (450-500 ml), was added. After two ether extractions, two washings of the ether extract with water, and subsequent drying ( $\text{MgSO}_4$ ) of the ether solution followed by solvent removal, 54 gm of an oil remained. This oil consisted of two components (80:20), as shown by GLC analysis on a silicone rubber column. The main fraction was found to be the desired aldehyde, while the smaller fraction consisted mainly of the starting material.

Purification of the reaction product either by chromatography on neutral alumina or via a bisulfite addition product was unsuccessful. Oxidations with silver oxide in aqueous base or in acetone at room temperature for 20 hours, or with Jones' reagent ( $\text{CrO}_3/\text{H}_2\text{SO}_4/\text{acetone}$ ) (163) were also unsuccessful.

Purification was best achieved by mixing 5-gm quantities of the oil with 12.5 ml of ethyl alcohol, 4 gm of Girard's T reagent (Fisher Scientific), and 1.25 ml of glacial acetic acid, followed by refluxing the mixture for 1 hour (112). To the cooled solution was added 40-50 ml of water, and the mixture thoroughly extracted with three portions of ether. (From these ether extracts, after washing with bicarbonate solution and water, small quantities of the starting alcohol could be recovered). To the aqueous layer was added 2.5 ml of concentrated hydrochloric acid and 25 ml of benzene, and the whole warmed gently on a steam bath for 30



minutes. The dried ether extract, freed from solvent, left 2.75 gm of a dark oil, which was shown by GLC to be fairly pure aldehyde ( $\sim 95\%$ ). Benzene elution of this contaminated aldehyde on neutral alumina resulted in a clear, yellow liquid of similar purity, but considerable quantities ( $\sim 40\%$ ) of the product were lost in this fashion.

The NMR and IR spectra of this compound are shown in Figs. 19 and 25 respectively.

Note - the use of Girard's T reagent (BDH) was found to be of detrimental value. Its use led only to tarry products, and gave none of the aldehyde.

A second method for preparing 2,2-dimethyl-1-acenaphthenecarboxaldehyde was found by applying the procedure of Corey and Chaykovsky (130) to 2,2-dimethyl-1-acenaphthenone.

Trimethyloxosulfonium iodide was prepared by refluxing a solution of 32 gm (0.41 mole) of dry DMSO and 60 ml of methyl iodide under nitrogen for 3 days, during which time the solution turned yellow and a white solid precipitated. The solid was filtered off, washed with chloroform; dried, and found to weigh 27 gm (30%). Recrystallization from 150 ml of water gave 24.3 gm of large colorless prisms, which were crushed and dried in a vacuum desiccator over phosphorus pentoxide.

Preparation of dimethyloxosulfonium methylide.

Sodium hydride (6.45 gm, 0.15 mole) as 56% dispersion in mineral oil was placed in a 3-neck, round-bottom flask equipped with a magnetic



stirrer. The hydride was washed three times with Skellysolve B, by swirling and decanting the liquid portion, in order to remove the mineral oil. The flask was immediately fitted with a reflux condenser, the system stoppered and evacuated. Immersion of the vessel in a warm water bath ( $\sim 50^\circ$ ) for 10 minutes enabled removal of the last traces of Skellysolve. The vacuum was broken, and one equivalent (33 gm, 0.15 mole) of powdered trimethyloxosulfonium iodide introduced through one of the side arms of the flask. The system was placed under nitrogen by evacuating and filling with nitrogen several times. Thereafter the system was opened to atmospheric pressure, and a slow influx of nitrogen maintained. One hundred ml of dry DMSO was introduced slowly over a 30-minute period via the dropping funnel, the solution being stirred throughout. A vigorous evolution of hydrogen ensued, and a milky-white mixture formed. This was stirred for a further 20 minutes.

Reaction of dimethyloxosulfonium methylide with 2,2-dimethyl-1-acenaphthenone.

To the above solution of the ylide, a solution of 16 gm (0.082 mole) of the ketone in 50 ml of DMSO was added, with stirring, over a 20-minute period. The mixture was heated at  $50-60^\circ$  for 4.5 hours, and then 250 ml of water was added. The reaction mixture was extracted with two portions of ether, and the combined ether extracts washed twice with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The yellow oil (15.8 gm) obtained was shown by NMR (Fig. 18) to be a 5:1 mixture of oxirane (CI) and starting ketone



respectively.

When only a 10% excess of methyllide was used and the mixture heated at 50-60° for 1 hour, a 3:2 ratio of oxirane to ketone was obtained. This ratio was raised to 2:1 when the reactants were allowed to stir at room temperature overnight and finally heated at 50-60° for 5 hours. A 10-hour heating period followed by overnight stirring caused decomposition of the products, the NMR spectrum of the products showing the presence of very little oxirane.

Heat was evolved when the above reaction products dissolved in Skellysolve B were placed on a column of 250 gm of neutral alumina. Elution with ether gave the original ketone, while methyl alcohol elution afforded 10.4 gm of crude 2,2-dimethyl-1-acenaphthenecarboxaldehyde (XCIX) as an orange oil. Nearly pure aldehyde was obtained as a pale-yellow oil (4 gm, ~30%) by rechromatography of the orange oil with benzene as eluant on neutral alumina.

The NMR and IR spectra (Figs. 19 and 25) support the assigned structure.

Reaction between 2,2-dimethyl-1-methyleneacenaphthene and perbenzoic acids.

To 3 gm (0.0155 mole) of 2,2-dimethyl-1-methyleneacenaphthene in 100 ml of chloroform at 0-5° was added during 1 hour a solution of perbenzoic acid (0.0183 mole) in chloroform (35 ml of a solution containing 0.072 gm of acid/ml of solvent, diluted with an additional 40 ml of chloro-



form). The reaction mixture was stirred at ice-bath temperature for 6 hours, and at room temperature for 10 hours. The solution was washed first with sodium bisulfite, then twice with 5% bicarbonate solution, and finally dried ( $\text{MgSO}_4$ ) and evaporated, leaving a dark-brown oil which became viscous and black in color when it stood at room temperature. The NMR spectrum showed the product to be mainly starting material, with no oxirane present (no signals at  $\tau=6.8$ ).

When a mixture of 2 gm (0.0103 mole) of the olefin in 70 ml of chloroform and 2.5 gm (0.0123 mole) of 85% m-chloroperbenzoic acid (FMC Corporation, Carteret, N.J.) in 50 ml of chloroform was stirred at 0° for 11 hours and then at room temperature for an additional 9 hours, a similar product was obtained, which contained none of the desired epoxy compound.

1,2,2-Trimethyl-1-acenaphthenecarboxaldehyde (C) was prepared in 84% yield by the alkylation of the corresponding 2,2-dimethylaldehyde, using excess methyl iodide and sodium hydride in benzene by the same method described for the methylation of 1-acenaphthenone (p. 190). The product was obtained by chromatography on neutral alumina, with Skellysolve elution removing all of the paraffin oil. Elution with benzene and finally with ether gave the trimethylaldehyde as a nearly pure, yellow oil. (Further purification, if necessary, could be achieved by treatment with Girard's T reagent, as described previously (p.207)). Upon cooling, the oil solidified and was recrystallized twice from ethyl alcohol. Nearly



colorless crystals were obtained, of which an analytical sample melted at 53-54°. Anal. Calcd. for  $C_{16}H_{16}O$ : C, 85.67; H, 7.19. Found: C, 86.02; H, 6.98. The NMR and IR spectra of this aldehyde are recorded in Figs. 20 and 26 respectively.

1,2,2-Trimethyl-1-acenaphthenecarboxaldehyde p-toluenesulfonyl-hydrazone (CII) was synthesized by refluxing for 4-5 hours a solution of 5.6 gm (0.025 mole) of the aldehyde with a slight excess of p-toluenesulfonylhydrazine in 100 ml of methyl alcohol. By placing the resulting reaction mixture in the refrigerator, 5 gm of nearly colorless crystals were deposited. These were collected by filtration and washed with ether. The filtrate was evaporated to a small oily residue, from which an additional 2.4 gm of solid was obtained by scratching, seeding, and chilling. The combined portions of crude hydrazone were washed with cold, 10% sulfuric acid in order to remove any unreacted hydrazine, and then purified by two recrystallizations as follows. Solution of the hydrazone in a minimum of hot methyl alcohol, dropwise addition of water till a faint cloudiness appeared, and subsequent cooling gave small, glistening white plates melting at 163.5-164.5°. Anal. Calcd. for  $C_{23}H_{24}N_2O_2S$ : C, 70.38; H, 6.16; N, 7.14; S, 8.17. Found: C, 70.17; H, 6.26; N, 7.28; S, 8.34.

The NMR spectrum is shown in Fig. 21. Addition of  $D_2O$  to the NMR sample and reintegration of the signals showed the N—H proton to be among the aromatic protons at 2.2-2.3 $\tau$ . The vinylic hydrogen also



was found buried in the aromatic signals, an observation reported elsewhere (164).

1-Hydroxymethyl-1,2,2-trimethylacenaphthene was prepared by the addition of 2.24 gm (0.01 mole) of trimethylaldehyde in 50 ml of ether to a solution of 0.40 gm (0.011 mole) of lithium aluminum hydride in 50 ml of ether. The mixture was refluxed for 3 hours, and stirred overnight at room temperature, followed by ethyl acetate-water decomposition. The inorganic salts were removed by filtration, the ethereal filtrate washed with water, dried ( $\text{MgSO}_4$ ), and evaporated to a yellow oil (2.15 gm). Chromatography on 50 gm of neutral alumina with ethyl acetate as eluant, followed by methyl alcohol elution, gave a combined yield of 2.04 gm of a pale-yellow liquid, which, when dissolved in Skellysolve B and chilled in a refrigerator, deposited a white, waxy solid. An analytical sample, prepared by subliming a small portion of the solid, gave a melting point of 65-66°. Anal. Calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}$ : C, 84.91; H, 8.02. Found: C, 85.08; H, 8.05.

The NMR spectrum of this compound is shown in Fig. 22.

The p-toluenesulfonate (CVI) was prepared by the method described on p.205 from 0.80 gm (0.00354 mole) of 1-hydroxymethyl-1,2,2-trimethylacenaphthene and 1.0 gm (0.0052 mole) of p-toluenesulfonyl chloride dissolved in 6 ml of pyridine, and allowed to stand at room temperature for 24 hours. The oil (1.25 gm) obtained after work-up was dissolved in methyl alcohol, from which 0.70 gm (52%) of small needles were obtained



on cooling. Recrystallization from a chloroform-ether (1:3) solution gave colorless crystals, m.p., 88-88.5° (decomp.). Anal. Calcd. for  $C_{23}H_{24}O_3S$ : C, 72.60; H, 6.36; S, 8.43; Found: C, 72.89; H, 6.36; S, 8.50. The molecular structure was supported by the NMR spectrum (Fig. 23).

1,1,2,2-Tetramethylacenaphthene (XCVIII) was obtained in 72% yield by the Wolff-Kishner reduction of the precursor, 1,2,2-trimethyl-1-acenaphthenecarboxaldehyde. A mixture of 1.25 gm (0.0056 mole) of the aldehyde, 5.5 ml of 85% hydrazine hydrate, and 5 ml of ethyl alcohol was refluxed for 1.5 hours. Addition of 6 ml of diethylene glycol was followed by removal by distillation of the lower-boiling components, until a temperature of 180° was reached. Then 0.77 gm (0.014 mole) of potassium hydroxide was added, the resulting mixture refluxed for 4.5 hours, cooled, diluted with water and extracted with ether. The ethereal extract was washed successively with dilute hydrochloric acid and water, then dried and evaporated. A light-brown oil (1.02 gm) remained which consisted of two components in a 15:85 ratio, as indicated by GLC analysis on a silicone rubber column. When cooled and scratched, the oil solidified. The solid was dissolved in ethyl alcohol, decolorized with Norit and allowed to crystallize, giving 500 mg of a yellow solid which was 98% pure by GLC, and melted at 43.5-44.5°. Sublimation at 0.5 mm pressure and at an oil bath-temperature of 90-100° produced a white solid, better than 99.5% pure melting at 57-58°. Anal. Calcd. for  $C_{16}H_{18}$ : C, 91.37; H, 8.63.



Found: C, 91.10; H, 8.51.

The NMR spectrum ( $\text{CCl}_4$ ) showed aromatic protons ( $\tau = 2.4-3.0$ ) and a sharp singlet ( $\tau = 8.75$ ) in the integrated area ratio of 1:2.

A pure picrate of the tetramethyl derivative could not be obtained.

Reduction of 1,2,2-trimethyl-1-acenaphthenecarboxaldehyde p-toluenesulfonylhydrazone with lithium aluminum hydride

Following the procedure of Caglioti and Grasselli (133), 6.1 gm (0.0156 mole) of the p-toluenesulfonylhydrazone in 150 ml of anhydrous THF (distilled from  $\text{LiAlH}_4$ ) was refluxed for 8 hours with 6 gm (0.16 mole) of lithium aluminum hydride. The cooled solution was poured slowly into moist ether, and was further decomposed with water and 10% sulfuric acid. After successive washings of the ether solution with 10% sulfuric acid, 10% sodium hydroxide, and water, the organic layer was dried ( $\text{MgSO}_4$ ) and freed from solvent, affording 2.3 gm of a yellow-brown oil. By GLC analysis on three columns, only three products were found, one in the amount of 5%, the other two being approximately equal ( $\sim 47.5\%$ ). By comparison of retention times with those of authentic samples, the latter two components were identified as 1,1,2-trimethylacenaphthene and 1,1,2,2-tetramethylacenaphthene. This observation was further supported by the NMR spectrum which showed three different methyl-signals ( $\tau = 8.67-8.88$ ) and a quartet centered at  $\tau = 6.78$ .

Lithium aluminum hydride reduction of 1-hydroxymethyl-1,2,2-trimethylacenaphthene p-toluenesulfonate.



Similar to a previous reduction (p.203), 1.12 gm (0.00295 mole) of the p-toluenesulfonate was treated with 0.50 gm (0.013 mole) of lithium aluminum hydride in a total of 125 ml of ether. The yellow oil (0.612 gm) which was obtained as the reaction product contained five constituents in the ratio of 4:3:12:5:76 (by GLC using a neopentylglycol succinate column at 200°). The main fraction was isolated by GLC and obtained as a pure liquid whose infrared spectrum (Fig. 27) possessed unsaturation at 1655 cm<sup>-1</sup>, and whose NMR spectrum (Fig. 24) contained a vinyl proton, showing allylic coupling to a methyl group, and in addition two other methyl groups. The data, which strongly suggests a structure such as 1,1,3-trimethylphenalene (CVII) was further supported by mass spectral data which showed a parent peak at m/e = 208, as well as strong peaks at m/e = 193 and 178, due to loss of one and two allylic methyl groups respectively. Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>: C, 92.26; H, 7.74. Found: C, 92.34; H, 7.75.

J. Experimental Work Concerned with the Preparation of Reduced Acenaphthenes

For the preparation of reduced acenaphthenes, the following reactions were carried out.

Following the procedure of Howell and Taylor (140), methyl acrylate (practical grade, 32 gm, 0.37 mole) was added to a boiling solution of sodium methoxide (1.5 gm in 8 ml of methyl alcohol) and indene (120 ml, 1.04 moles) during a period of 15 minutes. The solution was refluxed for



a further 40 minutes and then distilled under reduced pressure. After a fore-run of unchanged indene, methyl  $\beta$ -(3-indenyl)propionate (46.3 gm, 61% based on methyl acrylate) was collected at 131-133°/ 2 mm. Lit. b.p., 115-121°/1 mm (105).

By the method of Rapoport and Pasky (141), 75 gm of the above indenyl propionate in 125 ml of ethyl alcohol was reduced with 2 gm of 5% palladium on charcoal until hydrogen uptake (initial pressure 50 p.s.i.) was complete (less than 1 hour). After filtration and removal of the solvent, 71 gm (94%) of methyl  $\beta$ -(1-indanyl)propionate was distilled as a colorless oil at 113-114°/1.3 mm. Lit. b.p., 126°/2.5 mm (141).

A mixture of 204 gm (1 mole) of methyl  $\beta$ -(1-indanyl)propionate and 80 gm (2 moles) of sodium hydroxide in 720 ml of water was refluxed for 2.5 hours. The colorless, homogeneous solution was poured into cold, dilute hydrochloric acid. When cooled, the solution deposited  $\beta$ -(1-indanyl)propionic acid as a white solid. The air-dried solid was crystallized once from Skellysolve B and gave 175 gm (92%) of the acid of melting point 45-46°. Lit. m.p., 50° (57-59°) (55).

A solution of 171 gm (0.90 mole) of the acid and 200 gm (1.68 moles) of thionyl chloride in 500 ml of benzene was refluxed for 2.5 hours. The solution was stirred overnight at room temperature, then freed from solvent and excess thionyl chloride, and distilled under reduced pressure affording 122 gm (65%) of  $\beta$ -(1-indanyl)propionyl chloride as a nearly colorless oil, boiling at 120-122°/1.5 mm. Lit. b.p., 138-142°/11 mm (55).



2a,3,4,5-Tetrahydro-5-acenaphthenone (LII) was obtained in 96% yield by the procedure reported by Anderson and Wade (55). To 25 gm (0.12 mole) of  $\beta$ -(1-indanyl)propionyl chloride in 50 ml of dry benzene was added, in dropwise fashion, 68 gm (0.26 mole) of anhydrous stannic chloride in 60 ml of benzene. The mixture was stirred at room temperature for 2 hours, and then refluxed for 4 hours. The cooled solution was treated with ice and dilute hydrochloric acid, stirred for 10 minutes, and then the benzene layer separated. Washing of the organic portion with water and sodium bicarbonate, followed by drying and evaporation of the solvent, left 19.8 gm of crude, tan-colored ketone. Recrystallization from methyl alcohol gave a grey-brown solid, m.p., 85-87°. Lit. m.p., 85-86° (165).

2a, 3,4,5-Tetrahydroacenaphthene (CVIII) was prepared by the following two methods.

(1) By a Wolff-Kishner reduction (55), a mixture of 15 gm (0.087 mole) of the above ketone in 63 ml of ethyl alcohol containing 87 ml of 85% hydrazine hydrate was refluxed for 1 hour. Then 87 ml of diethylene glycol was added to the solution, and the alcohol and excess hydrazine distilled out of the mixture until the distillation temperature reached 170°. A further 11.7 gm (0.21 mole) of potassium hydroxide was added and the mixture refluxed for an additional 3 hours. Addition of cold water, extraction with ether, washing the extract with water, drying ( $\text{MgSO}_4$ ) and distillation yielded 3.7 gm (27%) of the required tetrahydroacenaphthene as a colorless



liquid. B.p., 90-91°/2.9 mm;  $n_D^{25}$ , 1.5560. Lit. b.p., 113.5-114°/10 mm;  $n_D^{25}$ , 1.5573 (142).

(2) Using the procedure of Johnson and Glenn (142) 30.8 gm (0.2 mole) of acenaphthene and enough ethyl alcohol to bring the total volume of suspension to 115 ml, was placed in an autoclave (volume of the bomb-257 ml) at room temperature. One-fourth teaspoon of Raney nickel catalyst (144) was added and hydrogen introduced to a pressure of 1009 p.s.i. (0.40 mole at 23°). The temperature was raised slowly to 110°, and the hydrogenation continued until the pressure remained constant. The product was worked up by filtration and vacuum distillation through a Vigreux column, and was obtained in 95% yield. B.p., 77-78°/1.0 mm;  $n_D^{24.5}$ , 1.5572.

The ultraviolet spectrum (95% ethyl alcohol) of 2a,3,4,5-tetrahydro-acenaphthene (Fig. 30) possessed a strong aromatic band at  $\lambda_{\max} = 208$  m $\mu$  ( $\epsilon = 14800$ ), and weak absorptions at  $\lambda_{\max} = 268$  m $\mu$  ( $\epsilon = 600$ ) and 276 m $\mu$  ( $\epsilon = 600$ ).

4-Bromo-2a,3,4,5-tetrahydro-5-acenaphthenone (CXI) was synthesized following a general bromination procedure (166). To 10 gm (0.058 mole) of tetrahydroketone in 125 ml of ether at 0°, 9.3 gm (0.058 mole) of bromine was added dropwise with stirring during a 30-minute period. When the addition of bromine was completed, the ice-water bath was removed and the reaction mixture stirred for an additional 30 minutes. The solution was poured into ice-water, extracted with ether, the ether layer washed with water and bicarbonate solution, then dried and evaporated.



A grey-brown solid (14.35 gm, 98%) remained, which was observed to be a lachrymator, possessing skin-irritating properties. A small portion was purified by steam distillation and recrystallization from methyl alcohol, m.p., 102-104°. Anal. Calcd. for  $C_{12}H_{11}BrO$ : C, 57.39; H, 4.42; Br, 31.82. Found: C, 57.63; H, 4.39; Br, 32.04.

Reaction between 4-bromo-2a,3,4,5-tetrahydro-5-acenaphthenone and 1,2-ethanedithiol.

A mixture of 5 gm (0.02 mole) of the bromo ketone in 25 ml of toluene, 50 mg of p-toluenesulfonic acid, and 1.88 gm (0.02 mole) of 1,2-ethanedithiol was refluxed for 21 hours, using a Dean-Stark (111) water-trap. A slight excess above the theoretical amount of water was collected, while hydrogen bromide was evolved in copious quantities. The cooled mixture was poured into water, extracted with ether, the ether extract washed with sodium bicarbonate solution and then dried and evaporated. The residual dark oil gave 5.5 gm of solidified material on cooling, which was extracted with 400 ml of hot methyl alcohol. The alcohol solution on cooling, deposited 3 gm of a pale-yellow solid, melting at 90-91°. By a Beilstein test, halogen was found to be absent. Anal. Calcd. for  $C_{14}H_{14}S_2$ : C, 68.24; H, 5.73; S, 26.03. Found: C, 68.37; H, 5.68; S, 26.36. A parent peak at  $m/e=246$  was observed in the mass spectrum. This is in agreement with a structure such as CXV.

Desulfurization (167) of 500 mg of this sulfur-containing compound in 50 ml of 98% ethyl alcohol with 10-15 gm of Raney nickel (144) during



15 hours of reflux, gave 2a,3,4,5-tetrahydroacenaphthene as the product, as determined by comparison of the NMR spectrum of the product with the spectrum of an authentic sample (three aromatic protons at  $\tau=3.0-3.3$ , and eleven methylene (and methynyl) protons between  $\tau=7.0-9.0$ ).

2a,3,4,5-Tetrahydro-5-acenaphthenol (CIX) was obtained in 93% yield by the addition of 15 gm (0.087 mole) of the corresponding ketone in 200 ml of ether to a solution of lithium aluminum hydride (6.6 gm, 0.174 mole) in 50 ml of ether. After addition was completed, a 2-hour reflux period followed, with subsequent decomposition of the mixture with moist ether, then water and 10% sulfuric acid. Recrystallization of the solid product from aqueous methyl alcohol gave a white solid, m.p., 95-96°. Lit. b.p., 158-160°/18 mm (141).

2a,3-Dihydroacenaphthene (CX) was prepared from 2a,3,4,5-tetrahydro-5-acenaphthenol by heating the latter (11.9 gm, 0.0684 mole) with 4.35 gm (0.0345 mole) of oxalic acid dihydrate. Both solids melted readily, and the solution was refluxed for 10-15 minutes. The mixture was cooled, extracted with ether, the ether layer washed free of any acid by sodium bicarbonate solution, then dried ( $\text{MgSO}_4$ ) and distilled. The desired product was obtained as a clear liquid (6.6 gm, 62%), boiling at 89-90°/1.9 mm;  $n_D^{25}$ , 1.5903. Anal. Calcd. for  $\text{C}_{12}\text{H}_{12}$ : C, 92.25; H, 7.75. Found: C, 92.32; H, 7.66.

The UV spectrum (95% ethyl alcohol, Fig. 31) supported the assigned structure, in which the double bond is in conjugation with the aromatic ring



(absorption at  $\lambda_{\max}=266\text{ m}\mu$ ,  $\epsilon=9250$  (see Table X, p.126 for comparison with styrene)). The IR spectrum (film) showed unsaturation at  $1623\text{ cm}^{-1}$ , while the NMR spectrum (Fig. 28) indicated an AB system, with vinyl protons at  $\tau=3.6$  and  $4.2$ .

An orange picrate was obtained (m.p. ,  $60-61^{\circ}$ ). Since it was unstable, decomposing quite readily on exposure to the atmosphere, a good elemental analysis could not be obtained.

#### Sodium-liquid ammonia reduction of acenaphthene.

A system composed of a 3-neck flask connected with a dry-ice condenser was flame-dried, while a current of dry nitrogen was passed through it. When cooled ( $\text{N}_2$ ), the condenser was charged with dry-ice and acetone, and 150 ml of liquid ammonia was collected in the flask. Following the procedure of Hückel and Schlee (145), 10 gm (0.065 mole) of acenaphthene, 40 ml of anhydrous ether, and 16 ml of absolute ethyl alcohol was added to the ammonia solution. The mixture was stirred vigorously while 3.0 gm (0.13 mole) of sodium was added in small pieces, during a period of 25 minutes, each piece being added when the green color due to the previous piece had been discharged. The decolorized solution was stirred for an additional 15 minutes, after which time the ammonia was evaporated on a water bath. In order to dissolve all the salts, 100 ml of water was added, and the resulting solution acidified with dilute hydrochloric acid. The liquid obtained from the ether extract, after removal of the ether, was analyzed by GLC (neopentylglycol succinate



column) and found to consist of 18% of starting material, 9% of 2a,3,4,5-tetrahydroacenaphthene (both identified by comparison of retention time with those of authentic samples), and 73% of 2a,5-dihydroacenaphthene.

The use of half the amount of sodium metal under the same conditions gave a 26:6:68 ratio of the above products, while the use of 20% excess metal resulted in a 4:12:84 distribution.

From the reaction of 20 gm (0.13 mole) of acenaphthene, 80 ml of ether, 32 ml of absolute ethyl alcohol, and 7.92 gm (0.345 mole, 33% excess) of sodium in 200 ml of liquid ammonia, the above mixture in a 3:14:83 ratio was obtained. Upon distillation of this mixture under reduced pressure, 17.9 gm of a colorless oil was obtained, b.p., 79.5-81°/1.2 mm, which contained only a trace of acenaphthene.

The oil was dissolved in 100 ml of carbon tetrachloride, and the solution cooled in an ice bath. With stirring, 16 gm (0.1 mole) of bromine was added dropwise during 30 minutes, each drop being rapidly decolorized. The evolution of some hydrogen bromide was observed. After the addition of bromine was completed, the solution was stirred for 20 minutes at 0°, during which time a white solid precipitated. A total of 22.5 gm of 3,4-dibromo-2a,3,4,5-tetrahydroacenaphthene was obtained by evaporation of the carbon tetrachloride solution. The solid was dissolved in ether, the ether solution washed with water and aqueous sodium bicarbonate, dried and evaporated. The dibromo compound was recrystallized three times from ether, and showed a melting point range of 105-125°. Anal. Calcd.



for  $C_{12}H_{12}Br_2$ : C, 45.60; H, 3.83; Br, 50.57. Found: C, 45.93; H, 3.43; Br, 51.00.

The dibromo compound (5 gm) in an ether solution was added to 20 gm of activated zinc dust (168) also in 200 ml of ether, and the mixture stirred vigorously at room temperature for 24 hours. After filtration and solvent removal, all of the original dibromo starting material was recovered unchanged.

2a,5-Dihydroacenaphthene (CXII) was prepared by treating 17.3 gm of the dibromo derivative with 1.7 gm (25-30% excess) of magnesium in the usual Grignard manner. The magnesium was placed in a flame-dried flask, to which a small amount of ether and dibromo compound were added. In order to initiate the reaction, a few drops of methyl iodide were introduced. The bromine compound, dissolved in a small amount of ether, was continuously added at such a rate that a brisk reaction occurred. After the addition was completed, the solution was refluxed for 2 hours, whereupon two layers separated. By careful addition of water and dilute hydrochloric acid the reaction mixture was worked up, yielding the dihydroacenaphthene containing a small amount of acenaphthene. After two fractional distillations through a short Vigreux column, 5.6 gm of a pure colorless oil was collected, b.p., 80-80.5°/1.25 mm.  $\eta_D^{24}$ , 1.5724. The liquid solidified on freezing, but melted near room temperature. Anal. Calcd. for  $C_{12}H_{12}$ : C, 92.25; H, 7.75. Found: C, 91.97; H, 7.74.



The dihydro compound possessed a parent peak at  $m/e = 156$  in its mass spectrum, and double bond absorption at  $1635\text{ cm}^{-1}$  in its infrared spectrum (film). The NMR spectrum showed the presence of two vinyl protons at  $\tau = 4.16$  (Fig. 29). The UV spectrum (95% ethyl alcohol, Fig. 32) was similar to that of 2a,3,4,5-tetrahydroacenaphthene as expected; strong absorption (aromatic) at  $\lambda_{\text{max}} = 205\text{ m}\mu$  ( $\epsilon = 14700$ ), and weak bands at  $266\text{ m}\mu$  ( $\epsilon = 500$ ) and  $273\text{ m}\mu$  ( $\epsilon = 500$ ).

The orange picrate was unstable, and decomposed readily.

K. The Stability of the Dihydroacenaphthenes

(1) 2a,3-Dihydroacenaphthene

(i) Thermal stability

2a,3-Dihydroacenaphthene was injected into a GLC column (silicone rubber) at  $200^{\circ}$ , and the outlet gases condensed and collected. Reinjection of the collected material gave the same retention time as was observed for the first injection, while the NMR spectrum also indicated the presence of only starting material.

(2) 2a,5-Dihydroacenaphthene

(i) Thermal stability

2a,5-Dihydroacenaphthene was injected into a neopentylglycol succinate column at  $190\text{--}200^{\circ}$  as described above in (1), and found to be stable under these conditions.

(ii) Base - catalyzed isomerization



A mixture of 210 mg of 2a,5-dihydroacenaphthene and 400 mg of sodium methoxide in 10 ml of methyl alcohol was refluxed for 1 hour. The solution was acidified with dilute hydrochloric acid and extracted with ether. Only starting material was found present in the ether solution as shown by the NMR spectrum of the product obtained after removal of the ether.

In a second experiment, 330 mg of the olefin and potassium tert-butoxide (from 0.5 gm of potassium and 10 ml of tert-butyl alcohol) was refluxed for 21 hours, and the reaction mixture worked up as described above. The NMR spectrum showed complete rearrangement to the conjugated olefin, 2a,3-dihydroacenaphthene.

(iii) Acid-catalysis

A mixture of the olefin (250 mg) and 500 mg of p-toluene-sulfonic acid in 10 ml of DME was refluxed and stirred for 20 hours. An ether extract of the mixture, washed with water, and dried and evaporated gave a product which, by NMR, showed that no rearrangement had occurred.

In order to prepare 4,5-dihydroacenaphthene (CXVII), the procedure of Treibs and Thörmer (139) was used. A quantity (112 gm, 0.71 mole) of 2a,3,4,5-tetrahydroacenaphthene was stirred at 70-75° for 4 days, while a stream of oxygen was bubbled through the solution by means of a gas dispersion tube. During the oxidation, the reaction mixture turned yellow, then yellow-orange in color, and also became very viscous. Since filtration through a sintered glass funnel was virtually impossible, the



mixture was extracted with Skellysolve B. From neither the Skellysolve extract nor the syrupy residue could any of the desired peroxide (CXVI) be isolated.

L. 1,8-Dimethylnaphthalene was prepared from acenaphthene by the following method.

By the procedure of Graebe and Gfeller (169), 25 gm of acenaphthene was dissolved in 300 ml of warm acetic acid. The temperature was adjusted to 80°, and 170-175 gm of sodium dichromate was added portion-wise with efficient stirring, care being taken that the reaction temperature did not rise above 85°. After complete addition of the dichromate (approximately 1 hour), the reaction mixture was refluxed for 2 hours, then poured into warm water, and the precipitate collected on Büchner funnel by suction filtration. The air-dried solid, naphthalic anhydride, weighed 26 gm (81%) and melted at 269-270°. Lit. m.p., 274° (169).

Following the directions by Boekelheide and Vick (170), 25 gm of naphthalic anhydride was added to a stirred slurry of 10 gm of lithium aluminum hydride in a mixture of 230 ml of absolute ether and 190 ml of dry benzene at a rate sufficient to maintain gentle boiling. After the addition was completed the mixture was boiled under reflux for an additional 12 hours. The excess lithium aluminum hydride was decomposed by the careful addition of water and the precipitated solid was collected. The inorganic salts were removed by washing the solid cake with dilute acid. The remaining solid was crystallized from a 50% solution of methyl alcohol



in benzene. This gave 15 gm (63%) of 1,8-dihydroxymethylnaphthalene, m.p., 158-159°. Lit. m.p., 157-158° (170).

1,8-Dimethylnaphthalene was obtained in poor yield by the hydrogenolysis of the above diol (171). Fifteen gm of the dihydroxy compound was dissolved in 300 ml of methyl alcohol. Five drops of concentrated hydrochloric acid was added and the hydrogenation carried out using platinum oxide at room temperature and low pressure (20 p.s.i.). Filtration from catalyst and concentration of the filtrate yielded a semi-crystalline residue. This residue was chromatographed on neutral alumina, using Skellysolve B as the eluant. The solid so obtained was recrystallized from 80-90% aqueous methyl alcohol, giving 1 gm of shiny plates, m.p., 61.5-62.5°. Lit. m.p., 62.5-64° (172).

The NMR spectrum ( $\text{CCl}_4$ ) showed a singlet at 7.18 $\tau$  for the two methyl substituents, along with aromatic signals between  $\tau=2.3-2.9$  (area ratio 1:1).

M. The Metalation of Acenaphthene. General Procedure for the Formation and Collection of Hydrogen Gas

The same procedure as used for indene and fluorene described on p.172 was employed in this case, with the exception that 0.05 mole of hydrocarbon was used instead of 0.10 mole. Following the period of reflux (see Table XI, p.129) the metal was removed as much as possible, and the reaction mixture decomposed with excess dilute hydrochloric acid.



The solution was extracted with ether, the ether extract dried ( $\text{MgSO}_4$ ), filtered and freed from solvent. The residual material was then analyzed by GLC, using three columns (see p.230). Column chromatography of the products on neutral alumina with Skellysolve B as eluant removed all the analyzable hydrocarbons (5.33-6.10 gm), while ether and methyl alcohol elutions removed polymer-like material (1.2-2.2 gm). Total material recovery was as high as 90-95%.

#### Metalation of acenaphthene at room temperature

By the procedure of Cram and Dalton (68) a solution of acenaphthene (0.782 gm, 0.00507 mole) in 100 ml of anhydrous DME was treated with 0.473 gm (0.012 gram-atom) of potassium. A dark-green color appeared on the surface of the metal almost immediately, and after 20 minutes the solution was almost black. A small piece of potassium was still evident even after the mixture had been stirred at room temperature for 17 hours. The metal recovered after this time weighed 0.056 gm. To the solution, freed from visible metal particles, was added 0.32 gm of water in 50 ml of DME in a dropwise manner. The black color changed to orange. The reaction mixture was then shaken with a mixture of water and pentane, the pentane layer washed with water, dried, filtered and evaporated to an oil. GLC analysis of three columns (see p.230) and NMR analysis showed the presence of four components: 11% of 2a,3,4,5-tetrahydro-acenaphthene, 21% of 2a,3-dihydroacenaphthene, 56% of acenaphthene, and 12% of an unidentified compound.



N. General Procedure for the Metalation and Methylation of Acenaphthene

The method as outlined for the metalation and methylation of the indenenes (p.174) was used here, with the exception that 0.05 mole of acenaphthene was employed and that a larger amount of methyl iodide (25 gm) was added. The results have been discussed under the appropriate heading in the Results and Discussion (p. 137 ). Column chromatography of the products on neutral alumina with Skellysolve B as eluant removed 6.3-7.6 gm of the analyzable hydrocarbons, while ether and methyl alcohol elutions removed 0.86-1.37 gm of polymer-like material.

O. Analysis of Acenaphthenes on GLC Columns.

The following 2.5 m columns were utilized for all GLC analyses: Silicone rubber, 25% by weight on Gas-Chrom P (60-80 mesh). This column separated the following groups of compounds from each other but failed to separate the individuals of each group where mixtures are indicated. (a) 2a,3,4,5-tetrahydroacenaphthene; 2a,3-dihydroacenaphthene; 2a,5-dihydroacenaphthene, (b) acenaphthene; 1-methylacenaphthene; 1,1-dimethylacenaphthene, (c) cis-1,2-dimethylacenaphthene; 1,1,2-trimethylacenaphthene, (d) 1,1,2,2-tetramethylacenaphthene.

Neopentylglycol succinate, 25% by weight on Gas-Chrom P (60-80 mesh).

This column separated the following groups from each other but not the individual members of each group. (a) 2a,3,4,5-tetrahydroacenaphthene, (b) 2a,3-dihydroacenaphthene; 2a,5-dihydroacenaphthene, (c) 1,1-dimethyl-



acenaphthene , (d) acenaphthene; 1-methylacenaphthene; 1,1,2-trimethyl-acenaphthene; 1,1,2,2-tetramethylacenaphthene , (e) cis-1,2-dimethyl-acenaphthene.

Apiezon L , 25% by weight on Gas-Chrom P (60-80 mesh). This column separated the following groups from each other but not the individuals contained in each group. (a) 2a,3,4,5-tetrahydroacenaphthene; 2a,3-dihydroacenaphthene; 2a,5-dihydroacenaphthene , (b) acenaphthene; 1-methylacenaphthene; 1,1-dimethylacenaphthene , (c) 1,1,2-trimethyl-acenaphthene , (d) cis-1,2-dimethylacenaphthene; 1,1,2,2-tetramethyl-acenaphthene.



BIBLIOGRAPHY

1. A. Baeyer and W. H. Perkin, Jr. Ber. 17, 122 (1884).
2. G. Krämer and A. Spilker. Ber. 23, 3276 (1890).
3. W. Marckwald. Ber. 28, 1501 (1895).
4. J. B. Conant and G. W. Wheland. J. Am. Chem. Soc. 54, 1212 (1932).
5. R. E. Dessy, Y. Okuzumi and A. Chen. J. Am. Chem. Soc. 84, 2899 (1962).
6. W. K. McEwen. J. Am. Chem. Soc. 58, 1124 (1936).
7. A. Streitwieser, Jr., W. C. Langworthy and J. I. Brauman. J. Am. Chem. Soc. 85, 1761 (1963).
8. A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons and A. H. Pudjaatmaka. J. Am. Chem. Soc. 87, 384 (1965).
9. E. C. Steiner and J. M. Gilbert. J. Am. Chem. Soc. 87, 382 (1965).
10. W. Marckwald. Ber. 33, 1504 (1900).
11. H. E. Fritz, D. W. Peck, M. A. Eccles and K. E. Atkins. J. Org. Chem. 30, 2540 (1965).
12. R. Weissgerber. Ber. 42, 569 (1909).
13. L. S. Walters. J. Soc. Chem. Ind. 46, 150 (1927); Chem. Abstr. 21, 2268 (1927).
14. K. Ziegler and O. Schäfer. Ann. 479, 150 (1930).
15. P. Lebeau and M. Picon. Compt. Rend. 173, 84 (1921); Chem. Abstr. 15, 3288 (1921); Compt. Rend. 175, 223 (1922); Chem. Abstr. 17, 3317 (1923).



16. H. Normant and B. Angelo. Bull. Soc. Chim. France, 354 (1960).
17. A. Melera, M. Claesen and H. Vanderhaeghe. J. Org. Chem. 29, 3705 (1964).
18. V. Grignard and C. Courtot. Compt. Rend. 152, 272 (1911); Chem. Abstr. 5, 1402 (1911); Compt. Rend. 154, 361 (1912); Chem. Abstr. 6, 1132 (1912).
19. C. Courtot. Ann. Chim. 4, 58 (1915); ibid. 5, 52 (1916); Chem. Abstr. 10, 2701, 2708 (1916).
20. Th. Zerewitinoff. Ber. 45, 2384 (1912).
21. D. Ivanoff and I. Abdouloff. Compt. Rend. 196, 491 (1933).
22. O. Blum-Bergmann. Ann. 484, 26 (1930).
23. W. Schlenk and E. Bergmann. Ann. 463, 227 (1928).
24. L. S. Miller. Doctoral Dissertation, Iowa State College, 1950; Org. Reactions, Vol. VIII, 296 (1954).
25. O. F. Beumel, Jr., and R. F. Harris. J. Org. Chem. 30, 814 (1965).
26. H. Gilman and R. D. Gorsich. J. Org. Chem. 23, 550 (1958).
27. J. J. Eisch and W. C. Kaska. J. Org. Chem. 27, 3745 (1962).
28. H. O. House and V. Kramar. J. Org. Chem. 27, 4146 (1962).
29. G. W. H. Scherf. Ph.D. Thesis, University of Alberta, Edmonton, 1961.
30. G. W. H. Scherf and R. K. Brown. Can. J. Chem. 38, 697, 2450 (1960); ibid., 39, 799, 856, 1388, 1613 (1961).
31. J. Thiele and A. Bühner. Ann. 347, 249 (1906).



32. C. Courtot. Compt. Rend. 160, 523 (1915); Chem. Abstr. 9, 1745 (1915).
33. J. Thiele and K. Merck. Ann. 415, 257 (1918).
34. W. Wislicenus and W. Hentrich. Ann. 436, 9 (1924).
35. C. K. Ingold and H. A. Piggott. J. Chem. Soc. 123, 1469 (1923).
36. C. K. Ingold. Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, N.Y. 1953. p. 546-547.
37. M. J. S. Dewar. The Electronic Theory of Organic Chemistry. Clarendon Press, Oxford. 1949. p. 193.
38. C. F. Koelsch and R. A. Scheiderbauer. J. Am. Chem. Soc. 65, 2311 (1943).
39. T. L. Yarboro, C. Karr, Jr. and P. A. Estep. J. Chem. Eng. Data, 6, 421 (1961).
40. H. Cristol and F. Plenat. Bull. Soc. Chim. France, 1325 (1962).
41. G. Bergson and A. Weidler. Acta. Chem. Scand. 17, 862, 1798, 2691, 2724 (1963); ibid. 18, 1483, 1487, 1498, 2003 (1964); Arkiv Kemi, 21, 187 (1964).
42. J. C. Winter, D. D. Godse and P. K. Gessner. J. Org. Chem. 30, 3231 (1965).
43. S. Friedman, M. L. Kaufman, B. D. Blaustein, R. E. Dean and I. Wender. Tetrahedron, 21, 485 (1965).
44. a) Chemistry of Carbon Compounds, Vol. IIIB; Edited by E. H. Rodd; Elsevier Publishing Co., Amsterdam. 1956. p. 1252-1273.



- b) ibid., p. 1461-1475.
45. a) Elsevier's Encyclopaedia of Organic Chemistry, Vol. 12A, Series III. Elsevier Publishing Co., Amsterdam. 1948. p. 88-419.
- b) ibid., Vol. 13, Series III. p. 133-190.
46. W. H. Perkin, Jr. and G. Rëvay. J. Chem. Soc. 65, 228 (1894).
47. W. S. Johnson. Org. Reactions Vol. II, 114 (1944).
48. C. F. Koelsch, H. Hochmann and C. D. Le Claire. J. Am. Chem. Soc. 65, 59 (1943).
49. M. T. Bogert and D. Davidson. J. Am. Chem. Soc. 56, 185 (1934).
50. K. N. Campbell, B. K. Campbell and M. J. McGuire. Proc. Indiana Acad. Sci. 50, 87 (1940); Chem. Abstr. 35, 5872 (1941).
51. M. Schlosser. Angew. Chem. Intern. Ed. Engl. 3, 287, 362 (1964).
52. D. J. Cram. Chem. Eng. News, 41, #33, 92 (1963).
53. C. Berthelot. Compt. Rend. 63, 788 (1866).
54. C. Berthelot. Compt. Rend. 65, 507 (1867); F. K. Beilstein. Handbuch der Organischen Chemie. Springer-Verlag, Berlin. Vol. 5, 587 (1922).
55. A. G. Anderson, Jr. and R. H. Wade. J. Am. Chem. Soc. 74, 2274 (1952).
56. H. W. W. Ehrlich. Acta. Cryst. 10, 699 (1957).
57. A. I. Kitaygorodsky. Tetrahedron, 9, 183 (1960).
58. E. Berliner, D. M. Falcione and J. L. Riemenschneider. J. Org. Chem. 30, 1812 (1965).



59. L. D. Hayward and I. G. Csizmadia. *Tetrahedron*, 19, 2111 (1963).
60. A. Reissert. *Ber.* 44, 1749 (1911).
61. E. H. Rodd and F. W. Lynch. *J. Chem. Soc.* 2179 (1927).
62. S. D. Ross, M. Finkelstein and R. C. Petersen. *J. Am. Chem. Soc.* 80, 4327 (1958).
63. L. F. Fieser and J. Cason. *J. Am. Chem. Soc.* 62, 432 (1940);  
*Org. Syn. Coll. Vol. III*, 3 (1955).
64. J. F. Cairns and W. J. Hickinbottom. *J. Chem. Soc.* 870 (1962).
65. H. Gilman and R. L. Bebb. *J. Am. Chem. Soc.* 61, 109 (1939).
66. A. A. Morton, J. B. Davidson, T. R. P. Gibb, Jr., E. L. Little,  
E. F. Clarke and A. G. Green. *J. Am. Chem. Soc.* 64, 2250 (1942).
67. A. N. Pudovik and A. A. Muratova. *Uchenye Zapiski Kazan.*  
*Gosudarst Univ.* 113, no. 8, 7 (1953); *Chem. Abstr.* 49, 14448  
(1955).
68. D. J. Cram and C. K. Dalton. *J. Am. Chem. Soc.* 85, 1268 (1963).
69. A. J. M. Wenham and J. S. Whitehurst. *J. Chem. Soc.* 3857 (1956).
70. L. I. Zakharkin, O. Yu. Okhlobystin and K. A. Bilevitch. *Tetra-*  
*hedron*, 21, 881 (1965).
71. G. E. Coates. *Organo-Metallic Compounds*. Methuen and Co. Ltd.,  
London. 1956. p. 1-42.
72. J. L. Down, J. Lewis, B. Moore and G. Wilkinson. *J. Chem. Soc.*  
3767 (1959).
73. D. H. Eargle, Jr. *J. Org Chem.* 28, 1703 (1963).



74. J. F. Eastham and G. W. Gibson. J. Am. Chem. Soc. 85, 2171 (1963).
75. T. E. Hogen-Esch and J. Smid. J. Am. Chem. Soc. 87, 669 (1965).
76. J. A. Dixon, P. A. Gwinner and D. C. Lini. J. Am. Chem. Soc. 87, 1381 (1965).
77. H. F. Ebel. Tetrahedron, 21, 699 (1965).
78. E. de Boer and E. L. Mackor. J. Am. Chem. Soc. 86, 1513 (1964).
79. D. D. Elleman and S. L. Manatt. J. Chem. Phys. 36, 2346 (1962).
80. J. A. Elvidge and R. G. Foster. J. Chem. Soc. 590 (1963).
81. T. Schaefer and W. G. Schneider. Can. J. Chem. 41, 966 (1963).
82. M. J. S. Dewar and R. C. Fahey. J. Am. Chem. Soc. 85, 2704 (1963).
83. Van Nostrand's Scientific Encyclopedia, Third edition. D. Van Nostrand Co., Inc., Princeton, N. J. 1958. p. 1191.
84. I. E. Muskat and M. Herrman. J. Am. Chem. Soc. 53, 252, 260 (1931).
85. E. A. Braude, E. R. H. Jones and E. S. Stern. J. Chem. Soc. 396 (1946).
86. H. Lindlar. Helv. Chim. Acta. 35, 446 (1952).
87. R. B. Wagner and H. D. Zook. Synthetic Organic Chemistry. John Wiley and Sons, Inc., New York. 1953. p. 46.
88. a) R. T. Morrison and R. N. Boyd. Organic Chemistry. Allyn and Bacon, Inc., Boston. 1959. p. 778.



b) ibid. p. 122.

89. S. Lindenbaum. Ber. 50, 1270 (1917).
90. J. A. Barltrop, R. M. Acheson, P. G. Philpott, K. E. MacPhee and J. S. Hunt. J. Chem. Soc. 2928 (1956).
91. W. E. Parham, H. E. Reiff and P. Swartzentruber. J. Am. Chem. Soc. 78, 1437 (1956).
92. P. A. Plattner, A. Fürst and K. Jirasek. Helv. Chim. Acta. 30, 1320 (1947).
93. R. A. Barnes and B. D. Beitchman. J. Am. Chem. Soc. 76, 5430 (1954).
94. A. J. Birch and H. Smith. Quart. Rev. 12, 17 (1958).
95. R. West and W. H. Glaze. J. Org. Chem. 26, 2096 (1961).
96. D. Bryce-Smith and A. C. Skinner. J. Chem. Soc. 577 (1963).
97. O. F. Beumel, Jr. and R. F. Harris. J. Org. Chem. 28, 2775 (1963).
98. A. Rembaum, A. Eisenberg and R. Haack. J. Am. Chem. Soc. 87, 2291 (1965).
99. F. Fichter and H. Stenzl. Helv. Chim. Acta. 22, 425 (1939).
100. J. J. Eisch and R. M. Thompson. J. Org. Chem. 27, 4171 (1962).
101. H. Cristol, F. Plenat and C. F. Huebner. Bull. Soc. Chim. France, 2640 (1964).
102. A. Bosch and R. K. Brown. Can. J. Chem. 42, 1718 (1964).
103. L. Bateman and J. I. Cunneen. J. Chem. Soc. 2283 (1951).
104. K. G. Hampton, T. M. Harris and C. R. Hauser. J. Org. Chem. 30, 61 (1965).



105. H. Dressler and R. J. Kurland. J. Org. Chem. 29, 175 (1964).
106. P. T. Lansbury and R. Thedford. J. Org. Chem. 27, 2383 (1962).
107. E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon and R. W. Stevenson. J. Am. Chem. Soc. 81, 4842 (1959).
108. N. D. Scott, J. F. Walker and V. L. Hansley. J. Am. Chem. Soc. 58, 2442 (1936).
109. A. Zweig and A. K. Hoffmann. J. Am. Chem. Soc. 84, 3278 (1962).
110. G. Stork and S. R. Dowd. J. Am. Chem. Soc. 85, 2178 (1963); Org. Syn. 41, 65 (1961).
111. K. B. Wiberg. Laboratory Technique in Organic Chemistry. McGraw-Hill Book Co., Inc., New York. 1960. p. 214.
112. L. F. Fieser. Experiments in Organic Chemistry, Third Edition. D. C. Heath and Co., Boston. 1955. p. 78-79, 88-89
113. M. Julia and M. Baillargè. Bull. Soc. Chim. France, 928 (1957).
114. B. R. Brown and D. L. Hammick. J. Chem. Soc. 1395 (1948).
115. E. J. Corey, D. J. Pasto and W. L. Mock. J. Am. Chem. Soc. 83, 2957 (1961); Tetrahedron Letters, 347 (1961).
116. C. E. Miller. J. Chem. Educ. 42, 254 (1965).
117. E. E. van Tamelen and R. J. Timmons. J. Am. Chem. Soc. 84, 1067 (1962).
118. G. Darzens and M. Dèlépine. Compt. Rend. 203, 1374 (1936); ibid. 204, 272 (1937).
119. A. H. Bone and L. A. Cort. J. Chem. Soc. 1986 (1962).



120. M. J. S. Dewar and R. C. Fahey. J. Am. Chem. Soc. 84, 2012 (1962); Angew. Chem. Intern. Ed. Engl. 3, 245 (1964).
121. M. Karplus. J. Chem. Phys. 30, 11 (1959); F. A. L. Anet Can. J. Chem. 39, 789 (1961).
122. W. E. Bachmann and J. C. Sheenan. J. Am. Chem. Soc. 63, 204 (1941).
123. R. Adams and A. F. Thal. Org. Syn. Coll. Vol. I, 107 (1941).
124. H. Gault and G. Kalopissis. Compt. Rend. 229, 624 (1949).
125. N. Maxim. Bul. Soc. Chim. France, 45, 1137 (1929); Chem. Abstr. 24, 2456 (1930).
126. G. G. Eberhardt. J. Org. Chem. 29, 643 (1964).
127. G. Zweifel and H. C. Brown. J. Am. Chem. Soc. 86, 393 (1964).
128. N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand and W. M. Weaver. J. Am. Chem. Soc. 79, 6562 (1957); ibid. 81, 4113 (1959).
129. D. H. R. Barton, B. J. Garner and R. H. Wightman. J. Chem. Soc. 1855 (1964).
130. E. J. Corey and M. Chaykovsky. J. Am. Chem. Soc. 87, 1345, 1353 (1965).
131. J. D. Roberts. Nuclear Magnetic Resonance. McGraw-Hill Book Co., Inc., New York. 1959. p. 58-60.
132. L. J. Bellamy. The Infrared Spectra of Complex Molecules. Methuen and Co. Ltd., London. 1958. p. 59, 156



133. L. Caglioti and P. Grasselli. Chem. Ind. 153 (1964).
134. B. E. Leggetter and R. K. Brown. Can. J. Chem. 42, 990 (1964).
135. E. L. Eliel. Record Chem. Progr. 22, 129 (1961).
136. J. A. Smith, H. Schechter, J. Bayless and L. Friedman. J. Am. Chem. Soc. 87, 659, 661 (1965).
137. P. K. Freeman and D. G. Kuper. J. Org. Chem. 30, 1047 (1965).
138. J. W. Wilt, J. M. Kosturik and R. C. Orlowski. J. Org. Chem. 30, 1052 (1965).
139. W. Treibs and J. Thörmer. Ber. 90, 94 (1957).
140. F. H. Howell and D. A. H. Taylor. J. Chem. Soc. 3011 (1957).
141. H. Rapoport and J. Z. Pasky. J. Am. Chem. Soc. 78, 3788 (1956).
142. W. S. Johnson and H. J. Glenn. J. Am. Chem. Soc. 71, 1087 (1949).
143. W. G. Dauben, R. P. Ciula and J. B. Rogan. J. Org. Chem. 22, 362 (1957).
144. R. Mozingo. Org. Syn. 21, 15 (1941).
145. W. Hückel and H. Schlee. Ber. 88, 346 (1955).
146. P. Lebeau and M. Picon. Compt. Rend. 159, 70 (1914); Chem. Abstr. 8, 3288 (1914).
147. W. Hückel, E. Vevera and U. Würffel. Ber. 90, 901 (1957).
148. R. M. Silverstein and G. C. Bassler. Spectrometric Identification of Organic Compounds. John Wiley and Sons, Inc., New York. 1963. p. 101.
149. R. A. Friedel and M. Orchin. Ultraviolet Spectra of Aromatic Compounds. John Wiley and Sons, Inc., New York. 1951. Spectrum no. 24.



150. G. J. Hoytink, E. de Boer, P. H. van der Meij and W. P. Weijland,  
Rec. Trav. Chim. 75, 487 (1956).
151. J. Smid. J. Am. Chem. Soc. 87, 655 (1965).
152. S. Bank and W. D. Closson. Tetrahedron Letters, 1349 (1965).
153. I. M. Heilbron and H. M. Bunbury. Dictionary of Organic Compounds.  
Eyre and Spottiswoode, London. 1953.
154. Buu-Hoi and R. Royer. Bull. Soc. Chim. France, 812 (1947).
155. J. Entel, C. H. Ruof and H. C. Howard. Anal. Chem. 25, 1303  
(1953).
156. K. Dziewoński and T. Lityński. Ber. 58, 2539 (1925).
157. M. D. Soffer, R. A. Stewart, J. C. Cavagnol, H. E. Gellerson and  
E. A. Bowler. J. Am. Chem. Soc. 72, 3704 (1950).
158. F. F. Blicke and R. F. Feldkamp. J. Am. Chem. Soc. 66, 1087  
(1944).
159. N. Lozac'h and Y. Mollier. Bull. Soc. Chim. France, 1243 (1950).
160. H. Rottendorf and S. Sternhell. Australian J. Chem. 16, 647 (1963).
161. S. C. J. Olivier and J. Wit. Rec. Trav. Chim. 56, 853 (1937).
162. N. G. Gaylord. Reduction with Complex Metal Hydrides. Inter-  
science Publishers, New York. 1956. p.855
163. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon.  
J. Chem. Soc. 39 (1946).
164. High Resolution NMR Spectra Catalog. Vol. I and II. Varian Associates,  
Palo Alto, California, Instrument Division. 1963. Spectra nos. 20,  
443, 485, 562.



165. J. v. Braun and J. Reutter. Ber. 59, 1922 (1926).
166. A. L. Wilds and J. A. Johnson, Jr. J. Am. Chem. Soc. 68, 86 (1946).
167. J. C. Craig, D. M. Temple and B. Moore. Australian J. Chem. 14, 98 (1961).
168. E. Baer and D. Buchnea. J. Biol. Chem. 230, 455 (1958).
169. C. Graebe and E. Gfeller. Ber. 25, 652 (1892).
170. V. Boekelheide and G. K. Vick. J. Am. Chem. Soc. 78, 653 (1956).
171. R. E. Beyler and L. H. Sarett. J. Am. Chem. Soc. 74, 1406 (1952).
172. L. H. Klemm and A. J. Kohlik. J. Org. Chem. 28, 2044 (1963).





**B29849**